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HIGH PRESSURE TECHNOLOGY

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BUILDING FOR THE FUTURE OF A PROFESSION

Fifteen prominent chemical engineers first met in New York more than thirty years ago to plan a continuing literature for their rapidly growing profession. From industry came such pioneer practitioners as Leo H. Baekeland, Arthur D. Little, Charles L. Reese, John V. N. Dorr, M. C. Whitaker, and R. S. McBride. From the universities came such eminent educators as William H. Walker, Alfred H. White, D. D. Jackson, J. H. James, J. F. Norris, Warren K. Lewis, and Harry A. Curtis. H. C. Parmelee, then editor of *Chemical & Metallurgical Engineering*, served as chairman and was joined subsequently by S. D. Kirkpatrick as consulting editor.

After several meetings, this Editorial Advisory Committee submitted its report to the McGraw-Hill Book Company in September, 1925. In it were detailed specifications for a correlated series of more than a dozen text and reference books, including a chemical engineers' handbook and basic textbooks on the elements and principles of chemical engineering, on industrial applications of chemical synthesis, on materials of construction, on plant design, on chemical-engineering economics. Broadly outlined, too, were plans for monographs on unit operations and processes and on other industrial subjects to be developed as the need became apparent.

From this prophetic beginning has since come the McGraw-Hill Series in Chemical Engineering, which now numbers about forty books. More are always in preparation to meet the ever growing needs of chemical engineers in education and in industry. In the aggregate these books represent the work of literally hundreds of authors, editors, and collaborators. But no small measure of credit is due the pioneering members of the original committee and those engineering educators and industrialists who have succeeded them in the task of building a permanent literature for the chemical-engineering profession.

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High Pressure Technology

EDWARD W. COMINGS

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McGRAW-HILL BOOK COMPANY, INC.

New York Toronto London

1956

EX, 82-385

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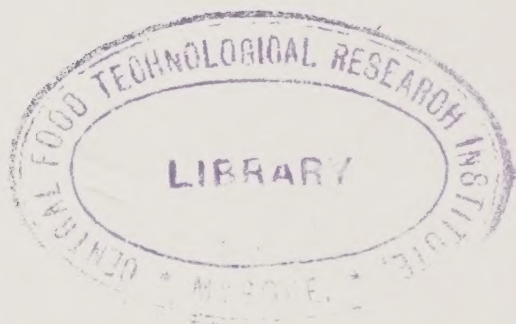
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HIGH PRESSURE TECHNOLOGY

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Library of Congress Catalog Card Number 55-11562

II



THE MAPLE PRESS COMPANY, YORK, PA.

To my wife

JEAN

*who doesn't seem to realize how much
of her is a part of what I do*

PREFACE

The number of chemical processes and separation operations carried out under elevated pressures has been increasing rapidly in recent years. The design of equipment for these purposes usually requires the application of somewhat more complex concepts than those required for operations at atmospheric pressure. Much of this design is based on sound scientific principles, but a considerable part depends on experience and is largely an art. This art may be described qualitatively on the basis of sound principles. This book makes use of scientific principles where they have been applied satisfactorily. These are supplemented with qualitative information where this has seemed more useful. Experimental or practical confirmation has been obtained in most cases.

The reader has been supposed to have the technical background of a senior undergraduate student in chemical engineering. By this means the book is restricted to a reasonable size, and undesirable duplication of material already available in many excellent texts on thermodynamics, chemical-engineering unit operations, physical chemistry, engineering mechanics, and the like, is avoided. Readers without an adequate background in these subjects as well as in the calculus and organic chemistry are referred to suitable textbooks.

The influence of elevated pressure on chemical and physical systems and on the design of equipment for handling these systems experimentally or on a commercial scale is the central theme. Individuals charged with handling such systems will find this information valuable. The book is also recommended as a class text. When used as a textbook, it is suggested that some sections be omitted. Parts of the chapters Chemical Processes, Equipment, and Experimental Techniques, for instance, are of greater value as reference material than as classroom exercises.

Chemical processes have been listed and are described briefly by R. Norris Shreve to point out the applications of the other chapters. An introduction to the principles which govern the properties of metals by H. C. Van Ness provides a basis for the selection and treatment of metals and alloys for use at high pressures. A large number of persons have contributed to the art of designing equipment. Every effort has been made to point out the salient features of a number of pieces of equipment

employed in work at high pressures. The reason behind the design is usually given. Only recently have carefully designed tests been made on thick-walled cylinders so that the theoretical analysis could be brought into agreement with actual behavior.

The physical and thermal properties of gases and liquids have been measured with great precision by scores of investigators. Selected examples of the techniques they have used are described. Both measured values and concepts of ideal behavior are used to interpret the effect of pressure on liquid and gaseous systems.

The author is grateful to Norman W. Krase for the legacy of a high-pressure laboratory and a course in high-pressure reactions at the University of Illinois. Starting without prior experience in high pressures, during fifteen years as teacher of the course and director of research in the laboratory the author collected much of the material for this book. This collection has been augmented and put into readable form in recent years at Purdue University. Only a small part is the original work of the author. W. P. Hagenbach made the calculations for several figures in Chap. 8. The contributions and suggestions of many others make up the major portion of the work. An attempt has been made always to acknowledge the original source. If in any case this has not been done, the author regrets the oversight.

E. W. COMINGS

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CHAPTER 1

INTRODUCTION

Pressure has an effect on chemical and physical processes. Some chemical processes become practical at high pressure when they would scarcely take place at atmospheric pressure. The synthesis of ammonia is such a process. In other cases, the course of a reaction or the rate at which it proceeds may be influenced by pressure so as to increase yields, reduce the amount of undesirable material formed with the product, and in other ways improve the economics of the process. The use of high pressures is not a panacea for all chemical reactions, and not all reactions will take place more readily at elevated pressures. Because of the high initial cost and high maintenance cost of pressure equipment, it is essential to exercise considerable care when determining whether a process should be carried out under pressure.

Such a decision involves understanding more than the effect of pressure on the chemical reaction. For instance, it may be practicable to use other raw materials and obtain the same products from a reaction at lower pressure. The pressure will also influence the choice of method for the purification of the reactants and for the recovery and purification of the products, as well as the design of the equipment used in the process. The pressure will have a bearing on the choice of process variables such as temperature, composition, and catalyst. These must be integrated to form a complete design for the process. A limited amount of experimental data and experience dealing with the physical, chemical, and thermal properties of the chemicals being processed and the materials of construction of the process equipment often provides the basis from which to start on the design of a new process. These data may be interpreted and applied to the design in the light of thermodynamics, reaction kinetics, the theory of catalysts, the mechanical principles of equipment design, economics, and safety.

It is well to realize that one does not force a process to take place. The control of a process consists rather in seeking out those conditions and requirements set by the process itself and then adhering meticulously to these in the design and operation of the equipment. No amount of brute

force or high pressure is likely to be so effective as simply finding and following the conditions and requirements which best suit the process.

1-1. Purpose of This Book. Thermodynamics permits the quantitative determination of the influence of pressure on chemical equilibrium and on the physical and thermal properties of a system. It indicates which measurements are required to do this. The design of a suitable closure or packing gland for use under high pressure, on the other hand, is much more of an art and is not always subject to precise calculation. It is the purpose of this book to present the methods of applying both science and art where each is most effective in high-pressure technology. It is not the purpose of the book to present the elementary principles of thermodynamics or of other scientific or engineering principles. The author was required to exercise his judgment concerning the extent to which the reader is expected to be familiar with the subjects treated. In some cases the reader will find the treatment too elementary, and in others too advanced. In the latter case, reference should be made to standard textbooks for additional background information.

The experience of many individuals has been collected to offer the reader a useful introduction to the art and science of carrying out chemical and physical processes at high pressure. Every effort has been made to present the reasons for each design or technique as well as its description. Of the work which has been reported in the literature, only a fraction could be included between the covers of this book. The reader may wish to consult the references included as footnotes for further information. The contributions of a few individuals to the knowledge of behavior at high pressures is worthy of special mention.

The extensive contributions of P. W. Bridgman comprise a voluminous literature by themselves. His work is summarized and reviewed in his book¹ and in a review article.² A. Michels³ has made a large number of precise measurements under high-pressure conditions. The book by Harold Tongue⁴ gave a comprehensive treatment of high-pressure design and construction two decades ago. Many of the designs he described are still common today. This was followed by the book by D. M. Newitt,⁵ which included the properties of common fluids under high

¹ P. W. Bridgman, "The Physics of High Pressure," The Macmillan Company, New York, 1931; *ibid.*, new impression with supplement, George Bell & Sons, Ltd., London, 1949.

² P. W. Bridgman, Recent Work in the Field of High Pressures, *Revs. Mod. Phys.*, **18**:1 93 (1946).

³ At the Van der Waals Laboratorium, Gemeente-Universiteit, Amsterdam.

⁴ Harold Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman & Hall, Ltd., London, 1934.

⁵ D. M. Newitt, "The Design of High Pressure Plant and Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.

pressure. The present book supplements and extends these earlier treatments and provides an integrated discussion of high-pressure technology, especially as it concerns the chemical engineer.

1-2. What the Book Contains. *Units and Dimensions.* The results of measurements at high pressures are expressed in the literature in many systems of dimensions and in many units. The value of these measurements is increased by an understanding of the relation between these various systems. Dimensions and units are the subject of Appendix A. This appendix should be consulted to avoid a misunderstanding of the units used in the book. A single system of units has not been adopted, but with the help of the appendix the various numerical values used may easily be converted to any system desired.

Glossary. A glossary is provided and serves to define and explain many of the technical and otherwise uncommon words and phrases used in the text. These words and phrases are not explained in the various chapters.

Processes. There are a large number of commercial and potentially commercial chemical processes employing high pressures. It is therefore not feasible to discuss each process in a comprehensive manner. Instead an extensive list of carefully chosen reactions has been prepared, and the conditions under which these take place, together with other information essential to the success of the process, are given briefly in the next chapter. The other aspects of high-pressure technology are then covered in the succeeding chapters. The last chapter returns to a single selected high-pressure chemical process and treats this in considerable detail. This is the synthesis of ammonia.

Design and Operation. The successful handling of high pressure in the laboratory or plant requires that one know something of the behavior of metals and be in a position to select suitable alloys. High on the list of essential information are the safety practices and habits that are a part of all successful operating techniques and are inherent in satisfactory designs for high-pressure use. A chapter devoted to safety is placed early in the book to emphasize its importance.

Much of the art of design of high-pressure apparatus has been collected and is arranged in an order which brings out the reason and good sense behind the design. This is followed by the more scientific analysis of stresses and strains in thick-walled cylinders. The mechanics of solids offers the analysis of other special cases, but the thick-walled cylinder is the most common shape used in high-pressure technology.

Physical Chemistry of Gases and Liquids. A few designs of special apparatus and of special techniques for making measurements at high pressure serve as an introduction to the problems involved in making such measurements. The chapter dealing with this subject is not compre-

hensive or uniformly representative. Experimental techniques similar to those described have provided the limited number of measurements available on the properties of liquid and gas under high pressures. A few of the numerical values for common gases are listed in Appendix D. The general behavior of gases and liquids is related by thermodynamics and other concepts and is covered in a separate chapter.

Chemical-engineering Unit Operations. Several of the chemical-engineering unit operations are carried out under high pressure. These include the flow of fluids, heat transfer, mass transfer, distillation, absorption, and adsorption. The high-pressure flow of gases and liquids through pipes or tubes, valves, fittings, orifices, and nozzles may be either viscous or turbulent, and in general follows much the same laws as at lower pressures. The fluid density and viscosity should be known or predictable under the conditions of flow. In the transfer of heat to or from fluids in pipes and in numerous other special cases, film coefficients may be predicted from the same correlation equations used at low pressures provided the physical and thermal properties of the fluid are known at the pressures employed.

Mass transfer occurs as an integral part of the chemical-reaction mechanism, and mass-transfer coefficients may be expected to vary in a manner paralleling those for heat transfer. Here the diffusivity is required in addition to density and viscosity. The absorption of certain gases such as carbon dioxide is carried out at higher pressures to take advantage of the increased solubility of the gas. Absorption of natural gasoline at high pressures avoids the cost of recompressing the lean gas for return to the wells in repressuring operations. In general, separation by distillation becomes less efficient as the pressure is increased. Nevertheless, distillation under pressure is frequently more economical than at atmospheric pressure because it allows the use of cooling water from natural sources in the condensers and avoids more expensive refrigeration. The amount of information which is applicable to these unit operations at high pressures is very limited.

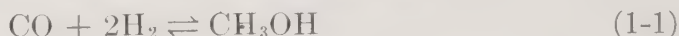
Chemical Equilibrium. When one or more compounds are held at constant temperature and pressure, they tend toward a stable equilibrium state. A single compound may decompose or rearrange itself to form one or more compounds. Two compounds may react. In some cases these reactions are unique and reversible and proceed to equilibrium in a short time. The equilibrium state can then be determined by experiment. To ensure that a true equilibrium has been reached in such experiments, an excess of the products of the reaction should be held under the identical conditions of temperature and pressure. If these form the same equilibrium state as the original reactants, this lends assurance that true equilibrium has been reached.

Frequently the reaction rate is so slow that equilibrium is not attained in a reasonable time or the products formed initially may themselves react and the situation becomes too complicated to identify an equilibrium state. Another complication arises when the initial reactants form several products by side reactions. These complications make it exceedingly difficult to determine equilibrium states experimentally. Such states may none the less be defined in spite of this inability to attain them. This is a hypothetical equilibrium. When an equilibrium results from a single reaction it supplies useful information. When it results from the more complicated consecutive and side reactions, more useful information is provided by the hypothetical equilibrium for the simple reaction alone. This equilibrium can often be calculated by thermodynamics. It is assumed that only the reaction or reactions under consideration take place and that the products do not react further but are available to aid in establishing the equilibrium. The concept of equilibrium as applied to a chemical reaction is useful in many ways. If the equilibrium can be shown to favor reaction, it should be possible for the reaction to take place at least partially. This is true even though the reaction has never been known to take place. The equilibrium state for given conditions establishes the maximum degree of completion for a reaction under those conditions. It thus allows comparison of the measured degree of completion of a reaction with that theoretically possible under the circumstances.

The equilibrium state can be varied according to the temperature, the pressure, the relative proportion of the reactants, and the presence of reaction products and inert constituents. Catalysts or inhibitors do not change the equilibrium state except in so far as they act as diluents or inert constituents. The quantitative influence of these conditions will be discussed later. The effect of these on the equilibrium is to be clearly distinguished from their effect on the rate of reaction, or the time required to approach the equilibrium state. The laws governing chemical equilibrium are exact and quantitative, while those for reaction kinetics or reaction rates are frequently empirical. Marked steps have been taken in recent years toward a more quantitative formulation of the principles of reaction kinetics. Both chemical equilibrium and reaction kinetics are of importance in the design of chemical reactors. These and other factors are considered in Chap. 11.

1-3. Functions of High Pressure. The preceding discussion makes it clear that pressure is a control variable, and in many cases elevated pressure may be useful in controlling a chemical reaction or in handling, storing, or separating chemicals. There are also situations in which elevated pressure is detrimental and its use is not indicated. The effects of higher pressure can be classified according to a number of specific functions.

Pressure may shift a chemical equilibrium, making possible a greater degree of completion of a desirable reaction or a lesser degree of completion of an undesirable side or consecutive reaction. Its function is then to direct the reaction into a preferred course. The methanol synthesis illustrates one of these effects. In the reaction



high pressure shifts the equilibrium to the right. This is the normal effect of pressure: to shift the equilibrium so that reaction results in a smaller volume of products than reactants. Pressure therefore favors this reaction, where the volume is reduced to one-third its initial value, to a greater extent than the side reaction



where the volume is reduced by a factor of one-half. Actually the equilibrium degree of completion of reaction (1-2) is negligible, and high pressure is required to increase the degree of completion of reaction (1-1). A side reaction to reaction (1-1) which has a very appreciable equilibrium degree of completion is that resulting in the formation of methane,



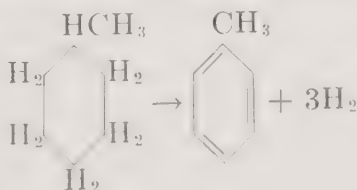
A combination of high pressure and a highly specific catalyst makes it possible for reaction (1-1) to proceed with a minimum of reaction (1-3) taking place. A crude alcohol can be made at 300 atm which contains 99.6 per cent methanol, 0.10 per cent higher alcohol, and the balance water. Practically no other organic reaction which is benefited by pressure will take place to the exclusion of all other reactions in the way the methanol reaction does. Other organic processes are complicated because of the fact that it is seldom possible to approach equilibrium in a single reaction. The effect of pressure on a number of factors must be taken into account. These include the equilibrium and reaction rate of the main reaction and of side and consecutive reactions, catalyst life, the purification of the reaction mixture, the separation of the desired products from the other products, and the possibility of recovering and recycling original reactants from the product stream.

The major use of pressure in connection with chemical reactions has been to shift the reaction equilibrium. This effect is no doubt the most clean-cut and the easiest to apply commercially. Pressure also affects the reaction rate. The increase in concentration when a gas mixture is put under pressure tends to increase the reaction rate and results in a greater capacity for a given reactor volume. Pressure may also decrease the reaction rate of heterogeneous reactions by saturating the catalyst sites with one reactant to the exclusion of others. Even in the case of

some liquid-phase organic reactions the rate has been observed to increase as much as five- to tenfold at pressures of 3,000 atm as compared with that at atmospheric pressure. Commercial applications have used pressures as high as 2,000 atm. The polymerization of ethylene is an example of a reaction carried out at such a pressure. Higher pressures can be used if these show commercial promise.

Another function of pressure is to maintain a liquid phase. There are both chemical and physical processes which depend on the presence of a liquid phase. When operating at high temperatures, or even at moderate or low temperatures with highly volatile components, it is necessary to keep the system under pressure to ensure the existence of the liquid phase. The hydrolysis or ammonolysis of monochlorobenzene to phenol or aniline, respectively, and also the liquid-phase cracking of petroleum fractions are examples of chemical reactions which require pressure to maintain a liquid phase. Likewise, in the separation of light hydrocarbons by distillation, the pressure ensures a liquid phase at normal temperatures. Pressure increases the solubility and is used in the separation of light hydrocarbons by the absorption process for this reason and to avoid the cost of recompression of the high-pressure gas from the wells. The increase in the solubility of carbon dioxide in water and of carbon monoxide in absorbents such as ammoniacal cuprous solutions is used to remove these gases in preparing the reaction mixture for the ammonia synthesis. The pressures needed to ensure a liquid phase will normally be less than the critical pressure. For pure compounds this ranges up to 65 atm for organic liquids and up to 218 atm for water. The pressures required for multicomponent mixtures may be much higher, extending to 500 and 600 atm in exceptional cases. Two phases may exist together within limits at pressures above the critical pressure of the mixture.

Increase in pressure frequently permits the operation of a catalytic process at a lower temperature, resulting in longer catalyst life. The hydroforming process for the production of toluene involves reactions such as the dehydrogenation of methyl cyclohexane



It has been found beneficial to carry out this reaction under pressure and in the presence of hydrogen; both would be expected to shift the equilibrium to the left. The effect on competing reactions and catalyst life apparently predominates over that on the main-reaction equilibrium.

CHAPTER 2

CHEMICAL PROCESSES

R. NORRIS SHREVE

During World War I, the use of pressure vessels to facilitate chemical processing received much stimulation by the suddenly precipitated demand for many chemicals previously imported from Germany. When dimethylaniline was to be manufactured in cast-steel autoclaves, many days had to be spent in laboriously peening to close the many small holes. Later during the same period dimethylaniline was made batchwise in long pipe autoclaves. Soon the United States petroleum industry perfected the continuous processing of their raw materials by pumping through a pipe autoclave. The American steel fabricators early learned to supply perfected tight pipes of steel and wrought iron. Used as continuous reactors even of only a few inches diameter, these were able to handle a surprising tonnage. Such pipe autoclaves are even now economical and applicable not only to petroleum but to other chemical processing. An example is the making of phenol from chlorobenzene and 18 per cent sodium hydroxide solution at 5,000 psi pressure. In this instance the pressure permits maintenance of the liquid phase at the elevated temperature needed to ensure an economical rate, conversion, and yield. Recent observations indicate that mutual solubility brings about a single phase at this elevated temperature and pressure.

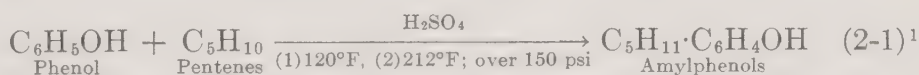
Erosion and corrosion must be guarded against by skillful and experienced design and selection. In the continuous-pipe pressure reactor, any bends must not be of too short a radius or erosion may be seriously aggravated. A minimum radius of 18 in. for 2-in.-diameter pipe, for 4,000- to 5,000-psi operating pressure, is frequently recommended. The selection of proper construction materials is based on experience checked by actual tests, often in the pilot plant. Materials used are steel, wrought iron, alloys like the various stainless steels, and lined pipes or vessels, using steel lined with 100 per cent silver, nickel, or tantalum.

These pressure processes are further employed to speed up solution, as of bauxite in caustic soda (100 psi), to minimize side reactions, and to increase catalyst life, as in hydroforming in the petroleum industry.

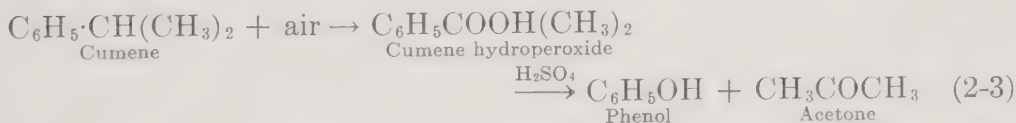
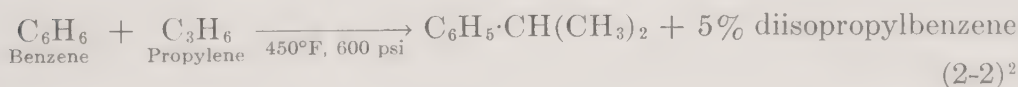
The principle of LeChatelier is one of the chief reasons for employing pressure to increase conversions and yields. The greater weight of a liquid passed through a given volume in comparison to the weight of vapors or gases below the critical points is another important basis for use of high pressures.

In this chapter selected chemical processes are presented, as well as their flow sheets. Processes were selected if they operated at 100 psi or higher. Certain processes are included which might under some circumstances employ a somewhat lower pressure. The individual process is arranged under the *unit-process* classification with the unit processes themselves in an alphabetical order. The Friedel-Crafts reaction, pertaining as it does to a series of reactions employing aluminum chloride or a similar product as a catalyst, is broken down and classified under the chemical change or unit process, e.g., alkylation, hydroformylation, or isomerization.

2-1. Alkylation. *Amylphenols.* The products are tertiary and secondary amylphenols, and the process may be carried out in two stages, obtaining first the tertiary product and then under more rigorous conditions, the secondary amylphenols. The alkylation autoclave is glass-lined.



Cumene, or Isopropylbenzene. This product has been important as a blending agent for aviation gasoline. However, it is the basic raw material for a new phenol process, for which the reactions are here included.

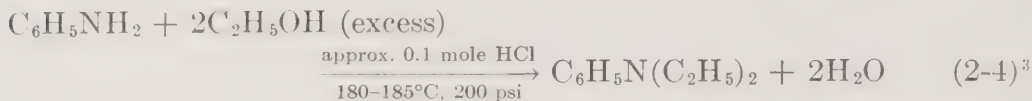


Diethylaniline. Sulfuric acid cannot be used as a catalyst because it would form ethyl ether from the alcohol. Ethyl chloride may be substituted for hydrochloric acid. The same procedure with 1 mole

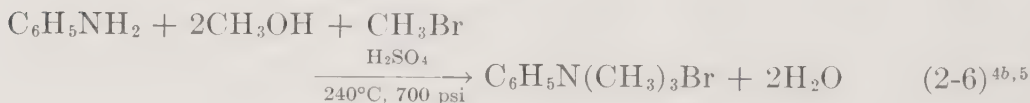
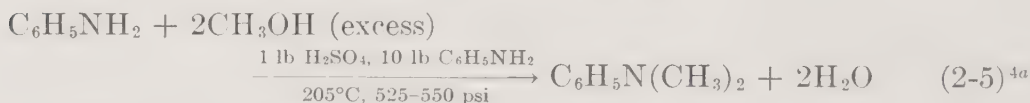
¹ For flow sheet see "Process Handbook," p. 159, The Gulf Publishing Company, Houston, 1953; or *Petroleum Refiner*, **32**(11):159 (1953).

² "Process Handbook," p. 157, The Gulf Publishing Company, Houston, 1953; or *Petroleum Refiner*, **32**(11):156 (1953).

alcohol is used for ethylaniline. Acidproof liners are required for the autoclave.

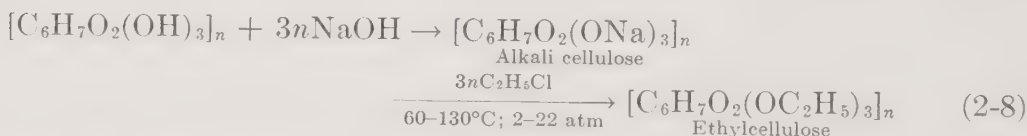


Dimethylaniline. Hydrochloric acid is not used because of its corrosive properties. The reaction is carried out in a steel autoclave. Side reactions lead to the formation of less than 1 per cent monomethylaniline. The quaternary ammonium salt and nuclear methylation products are formed at 250°C or with excessive acid. Most loss of methanol is due to formation of methyl ether which is blown off.

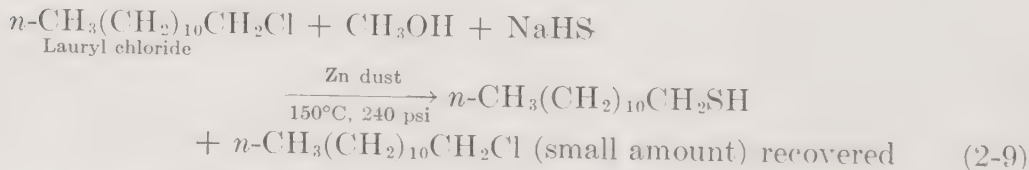


The Britton and Williams process, illustrated above, requires 16 hr with stirring in an iron autoclave. It uses 1 to 2 per cent methyl bromide by weight and avoids the ordinary by-products.

Ethylcellulose. Yield is 125 lb ethylcellulose from every 100 lb cellulose.^{4c,6}



Mercaptan^{4d}



2-2. Amination by Ammonolysis. 2-Aminoanthraquinone. Ammonia

³ P. W. Carleton and J. D. Woodward, U.S. patents 1,994,851, 1,994,852 (1935).

⁴ (a) P. H. Groggins, "Unit Processes in Organic Synthesis," 4th ed., p. 831, McGraw-Hill Book Company, Inc., New York, 1952; (b) *ibid.*, p. 806; (c) *ibid.*, pp. 824-826; (d) *ibid.*, pp. 844-845.

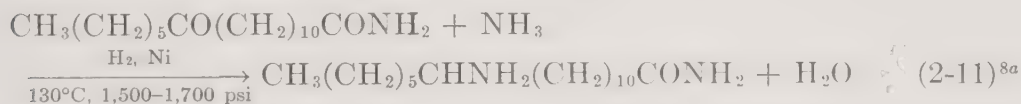
⁵ E. C. Britton and W. H. Williams, U.S. patent 1,794,092 (1931).

⁶ R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," pp. 539-540, Interscience Encyclopedia Company, New York.

is used in a 25:1 molar ratio to chloroanthraquinone in a horizontal, agitated, jacketed autoclave.

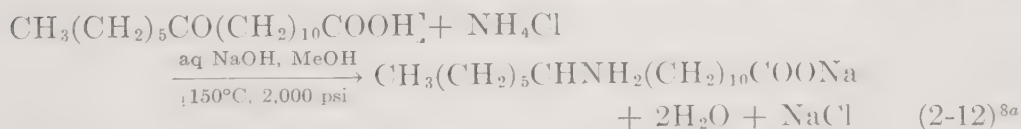
The reaction requires 24 hr at 200°C or 15 hr at 210°C in the presence of the oxidizing salts (these cause the product to be produced directly). The copper catalyst is not necessary. The leuco form of 1,4-diaminoanthraquinone may be obtained in the presence of sodium hyposulfite in 6 hr at 70 to 90°C using quinizarin as the starting material.^{9e}

12-Aminostearamide. The amination applies in general to ketones;⁷ it occurs in methanol solution.

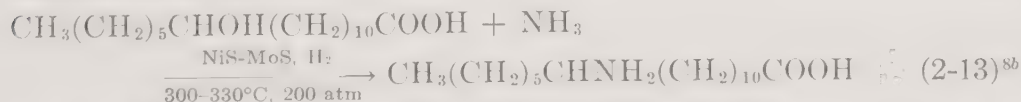


If the keto acid is used, enough alkali and water should be added to form the alkali soap (see 12-Aminostearic Acid).

12-Aminostearic Acid. The liquid-phase reaction requires 2 to 3 hr.



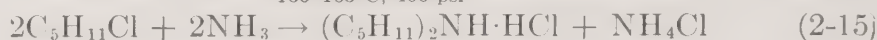
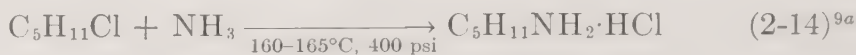
From stearic acid in stainless-steel autoclave, using 10 times ammonia, the yield is 90 per cent.



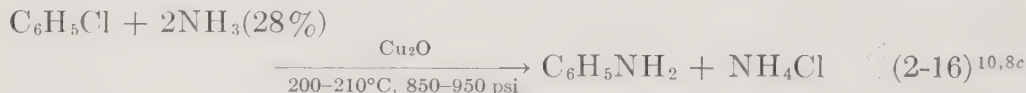
⁷ *FIAT Final Repts.* 716, 1081. Catalyst is 1 part WS₂ per 2 parts NiS at 80 to 160° and 2 to 3 atm with NH₃ ratio of 10:1 and a large excess of H₂.

* (a) Groggins, *op. cit.*, 3d ed., pp. 410-412; (b) *ibid.*, 4th ed., p. 408; (c) *ibid.*, pp. 397-398; (d) *ibid.*, p. 830; (e) *ibid.*, p. 366; (f) *ibid.*, p. 359; (g) *ibid.*, 3d ed., p. 403; (h) *ibid.*, 4th ed., pp. 398-403.

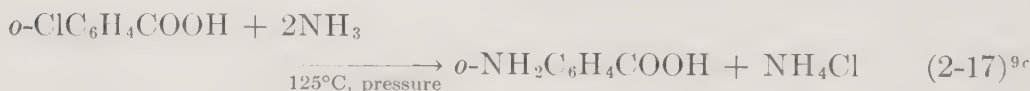
Amylamine. The reaction proceeds in the vapor phase, with side reactions including formation of some triamylamine, amylene, and amyl alcohol.



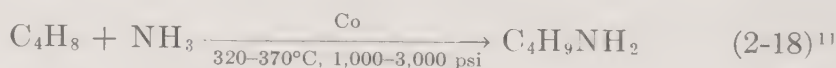
Aniline. A molar excess of ammonia over chloride of 5:1 is employed, and phenol and diphenylamine appear as by-products.



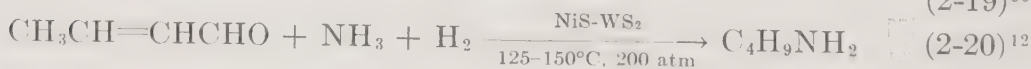
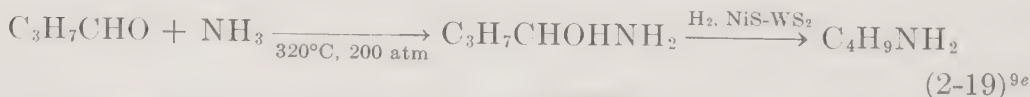
Anthranilic Acid. The reaction requires a catalyst.



Butylamine. Excess ammonia with olefins in general yields a mixture of amines, nitriles, and olefin polymerization products.



The following reactions are general for production of the lower alkylamines from saturated and unsaturated aldehydes and ketones.



With the proper catalyst, nitriles (Cu-Zn at 300 to 350°C may be used) or amines (NiS-WS₂-MoS may be used) may result from fatty acids also. Large excesses of ammonia and hydrogen are required, and alcohols may be used as diluents and solvents. Anhydrous ammonia is the

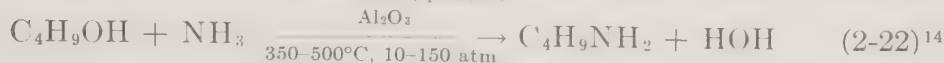
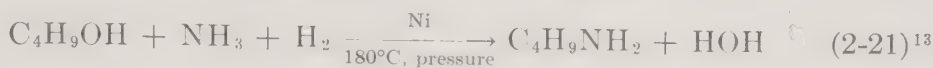
⁹ (a) Kirk and Othmer, *op. cit.*, vol. 1, p. 541; (b) *ibid.*, vol. 1, pp. 834-835, 917; (c) *ibid.*, vol. 2, p. 472; (d) *ibid.*, vol. 1, pp. 835, 950; (e) *ibid.*, vol. 1, pp. 835-836; (f) *ibid.*, vol. 1, pp. 670-671; (g) *ibid.*, vol. 5, p. 854; (h) *ibid.*, vol. 5, p. 877; (i) *ibid.*, vol. 6, p. 878; (j) *ibid.*, vol. 1, p. 837; (k) *ibid.*, vol. 1, p. 841; (l) *ibid.*, vol. 1, p. 840; (m) *ibid.*, vol. 1, pp. 833-834, 922.

¹⁰ N. H. Vorozhtzov and V. A. Kobelev, *J. Gen. Chem. (U.S.S.R.)* **4**:310 (1934).

¹¹ J. W. Teter, U.S. patents 2,381,470 to 2,381,473 (1945).

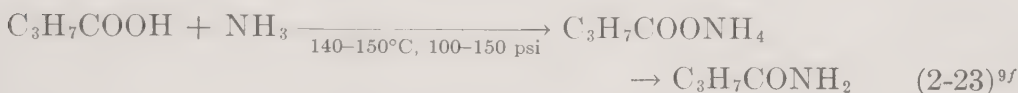
¹² C. T. Kautter, U.S. patent 2,051,486 (1936).

preferred reagent although the aqueous form may be used in some liquid-phase reactions. Alcohols are aminated as follows.

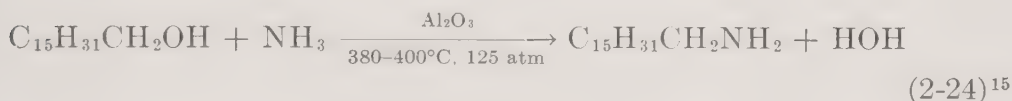


Molar excess of ammonia retards the formation of di- and trisubstituted ammonia derivatives; an excess is necessary in Eq. (2-21). Both reactions are general for alkylamines, the catalysts in the second being dehydrants and usually compounds of aluminum or phosphorus.

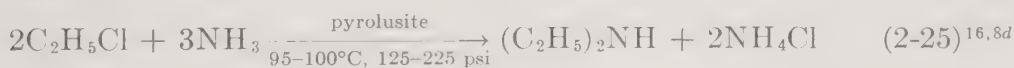
Butyramide. The following is the most general method for preparing primary amides with ammonia.



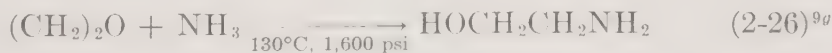
Cetylamine. Secondary and tertiary amines are formed as by-products, but the following is still the best method for production of amines of high-molecular-weight fatty alcohols.



Diethylamine. The liquid-phase-reaction products are extremely dependent on temperature, the monoalkylated amine being formed at 18°C , the dialkylamine at 56°C , ethanol at 80°C , and the trialkylamine at 90°C .



Ethanolamine. Ammonia is used in a 15:1 molar excess, and poly-substitution products occur in spite of this fact.



Ethylamine. Depending on the catalyst and on the ammonia-ether

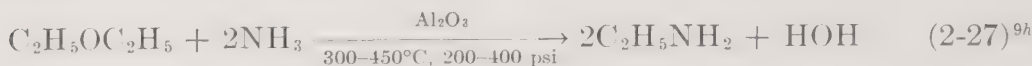
¹³ J. F. Olin and J. F. McKenna, U.S. patent 2,365,721 (1944).

¹⁴ P. Sabatier and A. Mailhe, *Comp. rend.*, **148**:898 (1909); Arnold, U.S. patent 1,799,722 (1931), reissue 19,362 (1935).

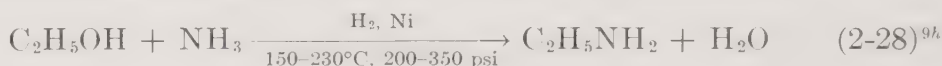
¹⁵ K. Smeykal, U.S. patent 2,043,965 (1936).

¹⁶ J. Schwyzer, "Die Fabrikation pharmazeutischer und chemischtechnischer Produkte," pp. 230-233. Springer-Verlag OHG, Berlin, 1931.

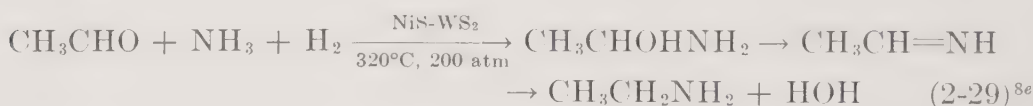
ratio, mono-, di-, or trisubstituted amines may be formed for the most part.



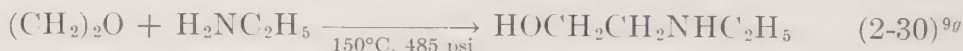
Polysubstitution products are again obtained in the following equation, the amounts depending on the molar excess of ammonia used.



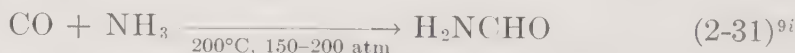
The following vapor-phase hydroammonolysis requires large excesses of both ammonia and hydrogen; in practice these excesses are recovered and recycled.



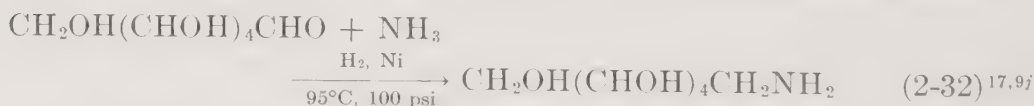
N-Ethylethanolamine. The amine is used in a 6:1 molar ratio to ethylene oxide, but polysubstitution occurs regardless.



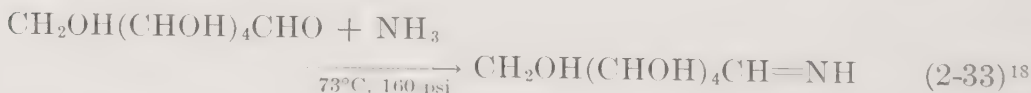
Formamide. Gases containing carbon monoxide may be used as well as the pure gas.



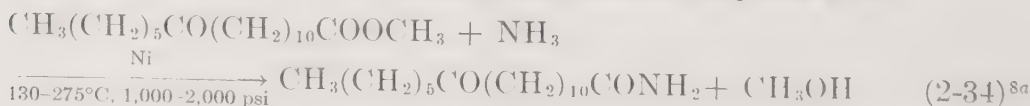
Glucosamine. The following reaction of aldose sugars with aqueous ammonia or alkylamines is general, and stable hydroxyamines result.



Glucosimine. Anhydrous ammonia in methanol condenses with aldose sugars.



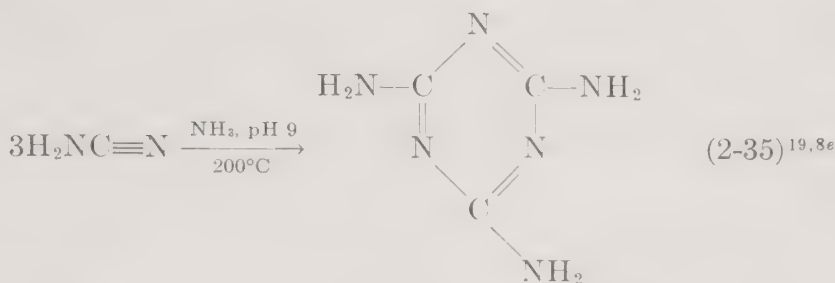
12-Kelostearamide. The liquid phase reaction requires 6 hr.



¹⁷ R. B. Flint and P. L. Salzberg, U.S. patents 1,994,467, 2,016,963 (1935).

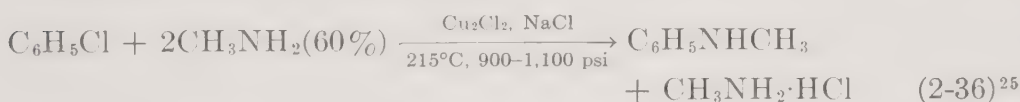
¹⁸ E. J. Lorand, U.S. patent 2,235,938 (1941).

Melamine. The trimer is believed to form through a guanidine intermediate.



The reaction is carried on under sufficient pressure to maintain the liquid phase. Two hours are required²⁰ at 155°C or the condensation may be carried out in better yields²¹ at 380°C; methanol^{22,23} or butanol²⁴ may be used as solvents. Pressures range up to 200 atm.^{9k}

N-Methylaniline. This pressure amination requires approximately 30 min and may be operated continuously. The reaction mass is treated with caustic to recover methylamine.

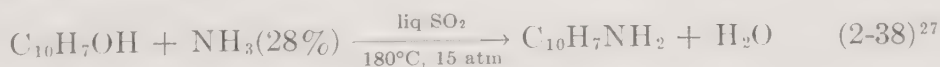


The entering methylamine-catalyst solution is saturated with salt. Optimum mole ratio of methylamine to chlorobenzene is 5:1.²⁶ The process has been suggested for aniline as well as methylaniline.

Morpholine. The reactants, dissolved in benzene, remain in a nickel-lined autoclave for 24 hr.



2-Naphthylamine. This liquid-phase Bucherer reaction requires 18 to 20 hr for completion.



¹⁹ W. H. Hill, R. C. Swain, and J. H. Paden, U.S. patent 2,252,400 (1941).

²⁰ W. Scholl and R. O. E. Davis, *Ind. Eng. Chem.*, **29**:202 (1937).

²¹ U.S. patents 2,164,706 (1939), 2,191,361 (1940), 2,287,597 (1942).

²² U.S. patents 2,301,629 (1942), 2,373,869 (1945).

²³ N. N. Hoover, *Chem. Eng.*, **57**:150 (1950).

²⁴ *FIOS Final Rept.* 1754, Item 22; *FIAT Final Rept.* 886.

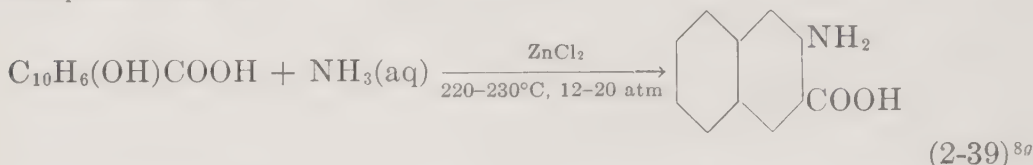
²⁵ E. C. Hughes, F. Veatch, and V. Elersich, *Ind. Eng. Chem.*, **42**:787 (1950).

²⁶ E. C. Hughes, U.S. patents 2,455,931, 2,455,932 (1948); E. C. Hughes and F. Veatch, U.S. patent 2,490,813 (1949).

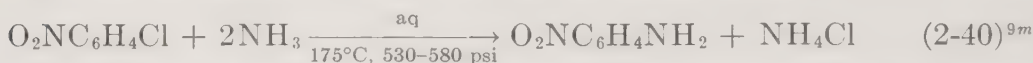
²⁷ *FIAT Final Rept.* 1313; I. G. Farben, Leverkusen.

The sulfite catalyst is believed to add to the keto form of the naphthol to form an intermediate in the reaction.²⁸

2-Naphthylamine-3-carboxylic Acid. The liquid-phase amination is complete in 24 hr.

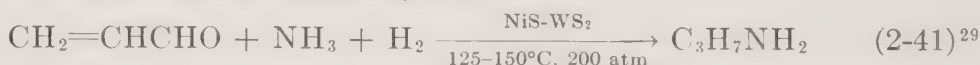


p-Nitroaniline. This batch amination employs a mole ratio of ammonia to nitrochlorobenzene of 15:1 in a well stirred autoclave.

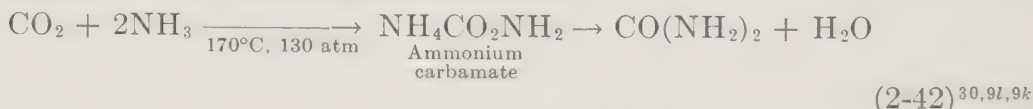


Reaction time is 16 hr, and 3 hr is required to bring the reactants to operating conditions. I. G. Farben developed a continuous process which operates at about 180°C and 200 atm.^{8h}

Propylamine. The reaction is general for unsaturated aliphatic aldehydes and yields normal primary amines.

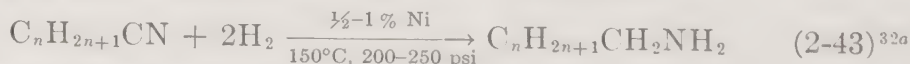


Urea. The exothermic amination is carried on in silver- or lead-lined, jacketed or continuous-pipe autoclaves.



If only 15 per cent excess ammonia is used, a 40 per cent conversion takes place, compared to 80 per cent when a 200 per cent excess of NH_3 is employed as in Fig. 2-10. The Pechiney process³¹ carries out the reaction in the presence of a circulating neutral oil carrying a slurry of recycle ammonium carbamate. The urea made dissolves in the water of reaction, is separated from the oil and ammonium carbamate, and is evaporated to solid form.

2-3. Amination by Reduction. *Alkylamines.* The nitrile, derived from a fatty acid, is slurried with Raney nickel and blown with hydrogen for 3 to 4 hr with stirring in a stainless-steel autoclave.



²⁸ W. Fuchs and W. Stix, *Ber.*, **55**:658 (1922).

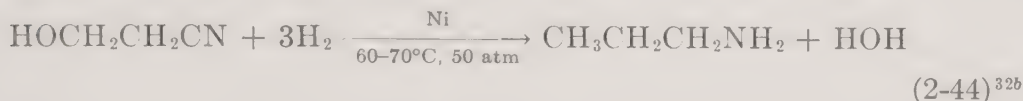
²⁹ C. T. Kautter, U.S. patent 2,051,486 (1936).

³⁰ W. L. E. Dewling and J. Robell, *FIAT Final Rept.* 889.

³¹ "Process Handbook," The Gulf Publishing Company, Houston, 1953; or *Petroleum Refiner*, **32**(11):176 (1953).

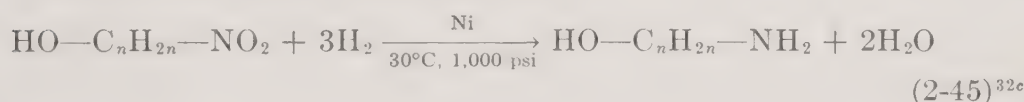
³² (a) Kirk and Othmer, *op. cit.*, vol. 6, p. 224; (b) *ibid.*, vol. 4, p. 759; (c) *ibid.*, vol. 9, p. 375.

The product is about 85 per cent primary amine, with a trace of the tertiary amine, and the remainder is secondary. Cyanohydrins may also be formed into amines in the following manner,

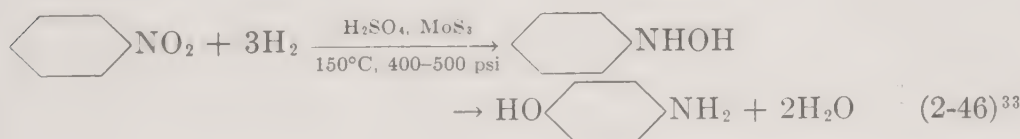


The liquid-phase reaction produces mixtures of primary, secondary, and tertiary amines.

Aminoalcohols. The Raney-nickel-catalyzed hydrogenation proceeds in methanol solution and gives good yields commercially under a wide variety of conditions for various alcohols.

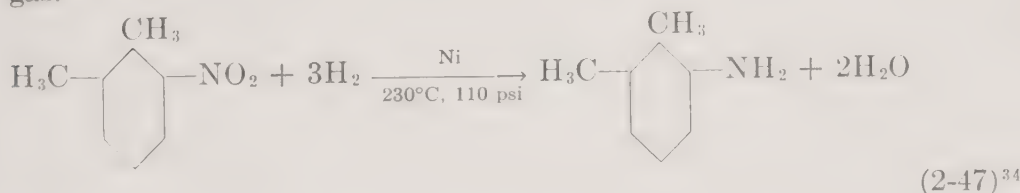


p-Hydroxyaniline. The liquid-phase reduction occurs in the presence of sulfides of cobalt, tungsten, and platinum as well as that of molybdenum.



Aniline is also produced, the yield being dependent on the catalyst composition. The reduction is general for nitro compounds containing no para substituents.

Xylidine. The liquid-phase reaction is carried out commercially with 3- and 4-nitroorthoxylenes and with purified hydrogen from synthesis gas.

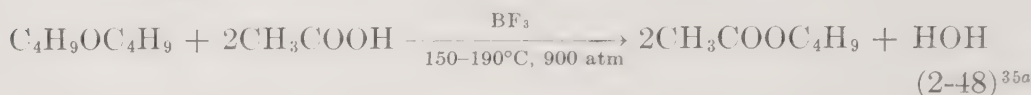


A ten-bed carbon-steel catalytic reactor is used. As is often the case, excess hydrogen is circulated in a mole ratio to nitroxylenes of 3:1.

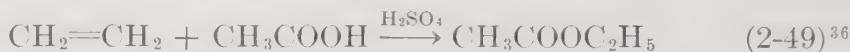
^{32b} C. O. Henke and J. V. Vaughn, U.S. patent 2,198,249 (1940).

³⁴ R. J. DeLargey, J. P. Okie, and L. M. Roberts, *Chem. Eng.*, **55**(10):124 (1948); G. K. Nelson, J. N. Wilson, and C. L. Raymond, *Chem. Eng. Prog.*, **45**:12 (1949); A. Voorhies, W. M. Smith, and R. B. Mason, *Ind. Eng. Chem.*, **40**:1543 (1948); C. L. Brown, W. M. Smith, and W. G. Scharmann, *Ind. Eng. Chem.*, **40**:1538 (1948).

2-4. Esterification. *Butyl acetate.* Acidic catalysts are required for the following reaction which occurs in the liquid phase.



Ethyl Acetate. According to Markovnikov's rule, pressure aids the addition which proceeds at room temperature or above and gives better yields with higher alkenes than with ethylene.

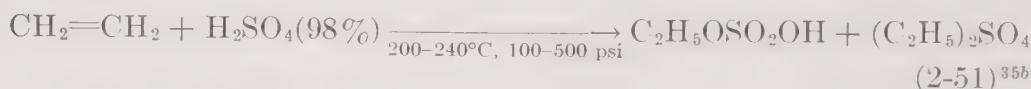


In general, esterifications with acid and alcohol proceed at higher rates with increased pressure.



Each atmosphere of pressure on the system raises the reflux temperature by about 20° , thus approximately quadrupling the rate of reaction.

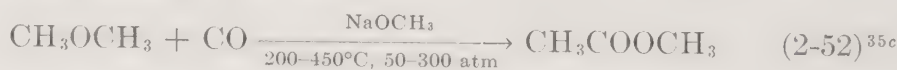
Ethyl Hydrogen Sulfate and Diethyl Sulfate. Very large quantities of these esters are made and hydrolyzed to ethyl alcohol and ether (see Fig. 2-2).



A similar esterification is practicable for a like step in the manufacture of isopropyl alcohol.

Isopropyl Hydrogen Sulfate. See Fig. 2-3.

Methyl Acetate. If the process occurs in the presence of water, the free acid is formed instead of the ester.



Methyl Formate. The liquid-phase reaction proceeds at high temperatures in the presence of acidic catalysts or metal alcoholates, the former catalysts giving yields of acetic acid.



Various other sets of conditions may be used with these reactants: 100 to 250°C , 500 to 900 atm, boron fluoride; 300 to 400°C , 100 to 700 atm, activated carbon with phosphoric acid (vapor); 200°C , 200 atm, charcoal

³⁵ (a) Kirk and Othmer, *op. cit.*, vol. 5, p. 807; (b) *ibid.*, vol. 5, 881; (c) *ibid.*, vol. 5, p. 807; (d) *ibid.*, vol. 3, p. 183, vol. 5, p. 787, vol. 9, p. 35.

³⁶ R. Altschul, *J. ACS*, **68**:2605 (1946).

³⁷ E. Cohen and H. F. G. Kaiser, *Z. physik. Chem.*, **89**:338 (1918).

³⁸ R. Wietzel and F. Kremp, U.S. patent 1,698,573; E. P. Bartlett, U.S. patent 2,341,420.

(vapor phase); 350°C, 700 atm, activated carbon with titania or alumina (again produces acetic acid).^{35d}

Rosin, Methyl Ester. The liquid-phase process has been adapted to a continuous reaction upon removal of water in towers.

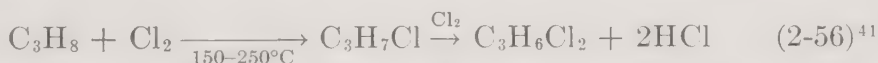


2-5. Halogenation. *Allyl Chloride, 3-Chloropropylene.* Two adiabatic reactors are provided in parallel so that carbon deposits can be removed from one while the other is in operation.



Low reaction temperatures favor addition to the double bond rather than substitution, but even at high temperatures some dichloropropane and dichloropropene are present as by-products.

Chloropropanes. Pressure is described as being superatmospheric, and a molar excess of alkane over chlorine of 10:1 is maintained in the chlorinator.



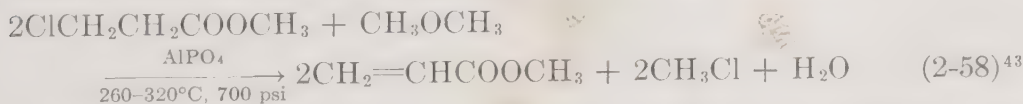
Mixtures of products are obtained, and an increase of pressure increases the relative rate of primary substitution.

2-Fluoroethanol. The reaction is carried on in a steel autoclave under pressure.



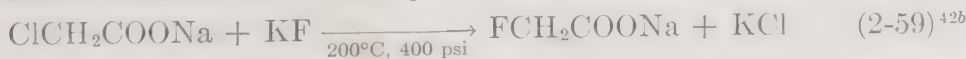
Substitution of ethylene chlorohydrin for ethylene oxide under the same conditions results in the same product, provided that potassium fluoride is used in place of hydrogen fluoride.

Methyl Acrylate. The dehydrohalogenation is general under these conditions for halogenated aliphatic acids, nitriles, or esters.



Aliphatic alcohols may be halogenated as well as ethers, and Al_2O_3 may be used as the halogen exchange catalyst (Cl-propanoic acid-methanol).

Sodium Fluoroacetate. The liquid-phase reaction requires 11 hr.



³⁹ E. West, Hercules Powder Company; J. A. Lee, *Chem. Eng.*, **55**:131-132 (1948).

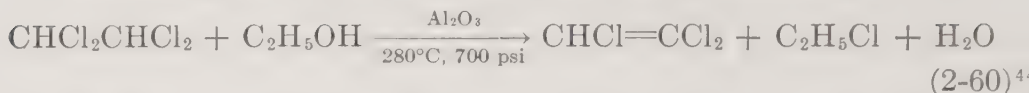
⁴⁰ A. W. Fairbairn, H. A. Cheney, and A. J. Cherniavsky, *Chem. Eng. Progr.*, **43**(6):280 (1947).

⁴¹ H. B. Hass and E. T. McBee, U.S. patent 2,105,733 (1938).

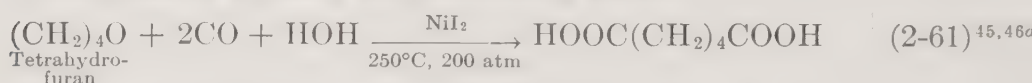
⁴² (a) Kirk and Othmer, *op. cit.*, vol. 6, p. 760; (b) *ibid.*, vol. 6, p. 764.

⁴³ L. Andrussow and G. Stein, U.S. patent 2,210,564 (1940).

Trichloroethylene. This is an example of halogen exchange.



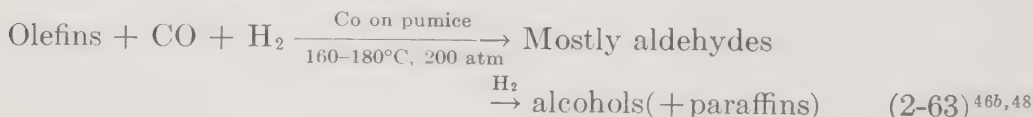
2-6. Hydroformylation, Carboxylation, and Carbonylation. *Adipic Acid.* The strongly exothermic reaction is commercially important and is typical of the reaction between dialkyl ethers and carbon monoxide in the presence of steam and condensing agents.



2,2,3-Trimethylbutyric Acid. Theoretical yields are obtained in 9.5 hr in this vapor phase in silver-lined autoclaves.



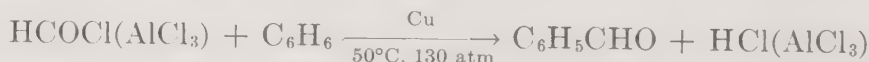
Aldehydes and (with H₂) Alcohols from Olefins (e.g., from 100 to 150°C Cut of Fischer-Tropsch Gasoline).



Benzaldehyde. A Friedel-Craft catalyst is used.

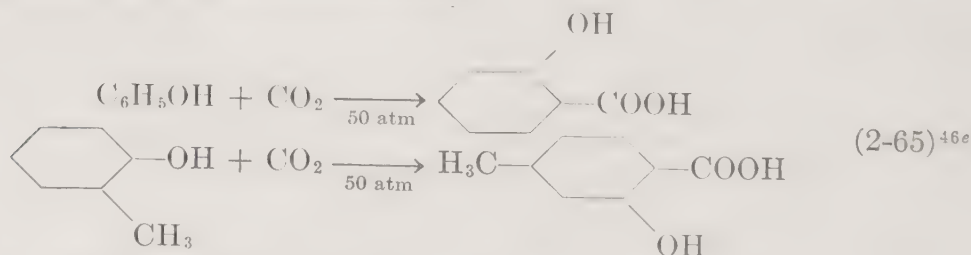


"Formyl chloride" may also be employed.



If nitrobenzene is used as a solvent, the reaction proceeds at atmospheric pressure.^{46d}

Benzoic Acids. Temperature and proportions of reactants affect the composition of the products obtained.



⁴⁴ L. Andrussow and G. Stein, U.S. patent 2,210,563 (1940).

⁴⁵ D. J. Loder, U.S. patent 2,135,453 (1938).

⁴⁶ (a) Groggins, *op. cit.*, 4th ed., p. 594; (b) *ibid.*, pp. 571-575; (c) *ibid.*, 3d ed., p. 744; (d) *ibid.*, 3d ed., p. 769; (e) *ibid.*, p. 742; (f) *ibid.*, p. 749.

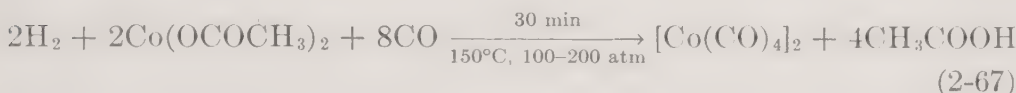
⁴⁷ T. A. Ford, H. W. Jacobson, and F. C. McGrew, *J. ACS*, **70**:3793 (1948).

⁴⁸ Flow chart of I. G. Farbenindustrie plant at Leuna.

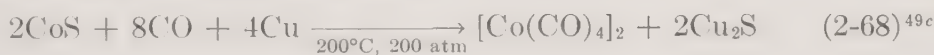
Cobalt Carbonyl Iodide. The carbonylation proceeds at room temperature.



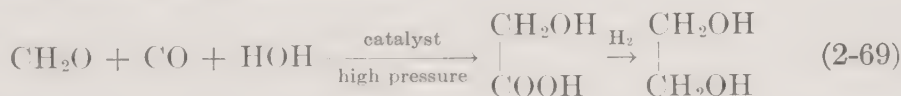
Dicobalt Octacarbonyl. The reaction occurs in ether, benzene, or toluene solution, and the product is used as a catalyst in the "Oxo" process,



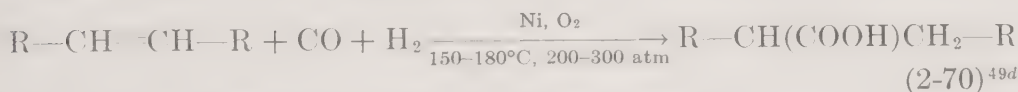
Water gas serves as the source of hydrogen and carbon monoxide, with almost any salt of cobalt acting as well as the acetate. The reaction occurs with cobalt carbonate at 180°C and 3,200 psi,^{49b} or with Raney cobalt and carbon monoxide under 3,200 psi and 150°C in ether.⁵⁰ Copper may be used in some cases,



Ethylene Glycol from Formaldehyde.

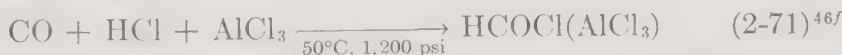


Fatty Acids. The reaction has been used for some time.

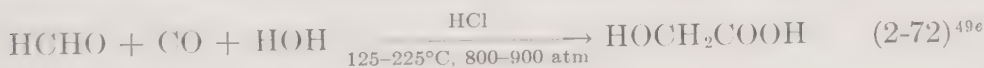


A C_{11} to C_{17} olefin cut is used as the raw material.

Formyl Chloride. The product serves as an intermediate in carbonylation reactions.



2-Hydroxyacetic Acid. The liquid-phase reaction takes place in an aqueous solution of sulfuric, hydrochloric, or phosphoric acids.



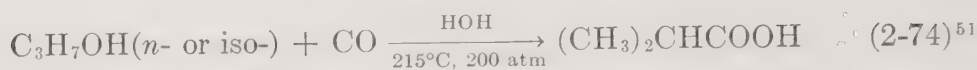
Isobutanol. This is a vapor-phase hydroformylation.



⁴⁹ (a) Kirk and Othmer, *op. cit.*, vol. 4, p. 203; (b) *ibid.*, vol. 4, p. 201; (c) *ibid.*, vol. 4, pp. 202-204, vol. 9, pp. 700-702; (d) *ibid.*, vol. 6, pp. 241-242; (e) *ibid.*, vol. 3, pp. 183-184; (f) *ibid.*, vol. 2, p. 678; (g) *ibid.*, vol. 6, p. 260; (h) *ibid.*, vol. 3, p. 184; (i) *ibid.*, vol. 6, p. 877; (j) *ibid.*, vol. 3, p. 183.

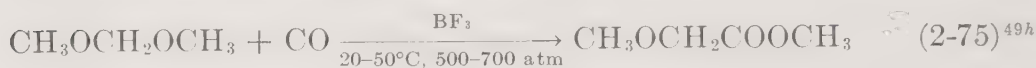
⁵⁰ H. Adkins and G. Krsek, *J. ACS*, 70:383 (1948).

Isobutyric Acid. This is a vapor-phase process.

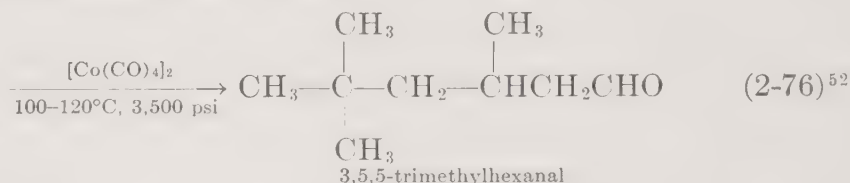


Isovaleric Acid. The product $[(\text{CH}_3)_2\text{CH}_2\text{CHCOOH}]$ is formed during the high-pressure synthesis of alcohols from carbon monoxide and hydrogen.^{49d}

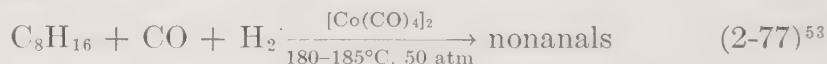
Methylmethoxyacetate. This is an acid-catalyzed liquid-phase reaction.



Nonanals. The commercial process provides a 90 per cent yield from diisobutylene in 20 to 30 min reaction time in benzene or toluene solution. $(\text{CH}_3)_3\text{CCH}=\text{C}(\text{CH}_3)_2 + \text{CO} + \text{H}_2$

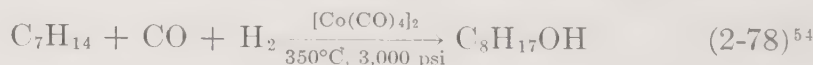


The raw material is readily available as a by-product in the petroleum industry, and the product is easily converted to products which have commercial value.



One-to-one synthesis gas serves as a source of carbon monoxide and hydrogen in the above liquid-phase process; alcohols are not formed because of the low partial pressure of hydrogen, but at higher pressures alcohols result.

Octanols. Feed to the countercurrent reactor contains the catalyst.



Two parallel reactors may be used at 150 to 200°C.⁵⁵

Oxalyl Chloride. This is another carbonylation intermediate.



⁵¹ D. V. N. Hardy, *J. Chem. Soc.*, 358 (1936).

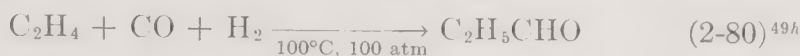
⁵² "Chemicals from the Oxo Process," Rohm and Haas Company, Philadelphia. Cf. Groggins, 4th ed., *op. cit.*, pp. 566-567, 575.

⁵³ I. Wender, R. Levine, and M. Orchin, *J. ACS*, **72**:4375 (1950).

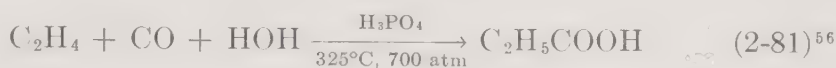
⁵⁴ Standard Oil Development Company, British patent application S360.

⁵⁵ P. T. Parker and G. O. Hillard, U.S. patent 2,571,160 (1951).

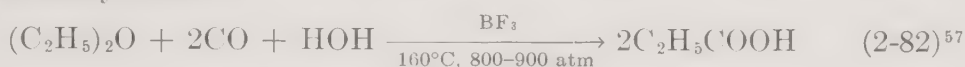
Propionaldehyde. The reaction is general for production of aldehydes, ketones, and alcohols, depending on the ratios of reactants present.



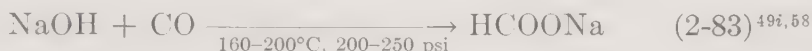
Propionic Acid. Feed to the vapor-phase reaction is 90 per cent carbon monoxide, 2 per cent ethylene, and 8 per cent steam; the catalyst is phosphoric acid on charcoal.



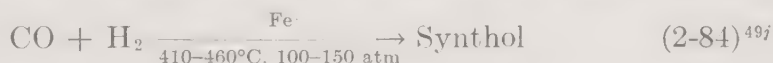
A product containing over 90 per cent propionic acid may be obtained from diethyl ether.



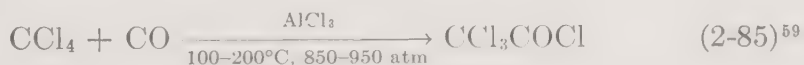
Sodium Formate. The liquid-vapor phase reaction may be carried out continuously.



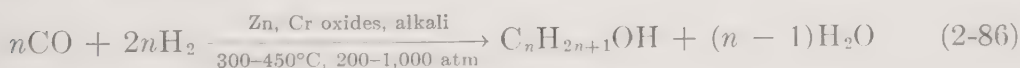
Synthol. A German process which operates in the vapor phase under the influence of alkali-promoted iron produces a complex mixture of alcohols, aldehydes, fatty acids, esters, and hydrocarbons called Synthol.



Trichloroacetyl Chloride. This is a Friedel-Craft-type hydroformylation.



2-7. Hydrogenation. *Alcohols.* Higher alcohols result from a synthesis similar to methanol using higher pressure and with the addition of alkali to the catalyst.



The product is a mixture of primary and secondary alcohols of from one to nine carbon atoms but with very little ethyl alcohol (see Fig. 2-4).

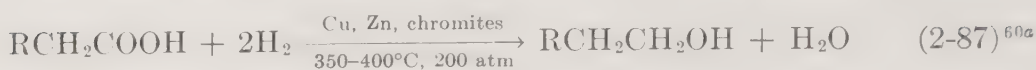
⁵⁶ G. B. Carpenter, U.S. patent 1,924,766 (1933).

⁵⁷ D. J. Loder, U.S. patent 2,170,825 (1939).

⁵⁸ F. Ullmann, "Encyklopädie der technischen Chemie," 2d ed., vol. 4, p. 9, Urban & Schwarzenberg, Berlin, Munich, Vienna, 1953.

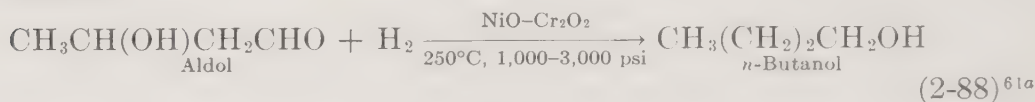
⁵⁹ C. E. Frank, A. T. Hollowell, C. W. Theobald, and G. T. Vaala, *Ind. Eng. Chem.*, **41**:2061 (1949).

Alcohols from Fatty Acids and Esters. See Lauryl Alcohol.



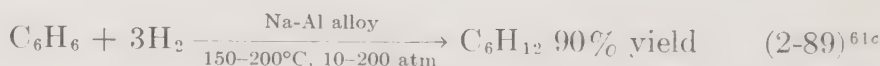
Ammonia. Ammonia synthesis is handled in detail in Chap. 12.

Butanol from Aldol. Commercial *n*-butanol is manufactured by this reaction.

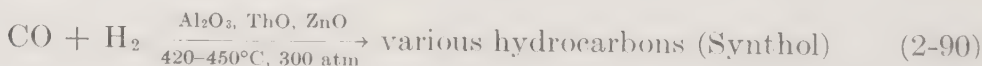


Coal hydrogenation has been carried out in two directions, one rather complete to break the coal molecule down to products in the motor-fuel range. Catalysts are iron and iron oxides, molybdenum, tungsten, and tin compounds at 350 to 500°C and 200 to 700 atm, with coal ground finely and pasted with a nonvolatile oil. Flow sheets and descriptions are available.^{60b,61b} The more promising process that is just being developed by Carbide and Carbon Chemicals Corporation dissolves the coal in a special aromatic solvent and, usually without a catalyst, subjects the coal to minimum breakdown, resulting in products of higher value.⁶²

Cyclohexane. This reaction is also run in reverse. It is carried out in the vapor phase.



Fisher-Tropsch Synthesis. At low pressure, the reaction furnishes hydrocarbons of lower octane number.



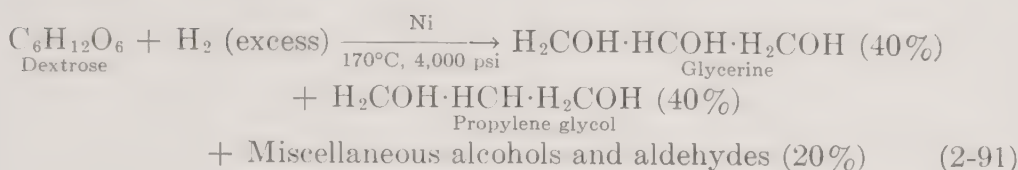
Glycerine from Dextrose from Starch. One hundred thousand dollars was spent upon details of this reaction by two separate organizations. One difficulty is maintaining the catalyst in suspension in a continuous-pipe autoclave; another is that the reaction does not furnish glycerine alone and the cost of separation increases the operating expenses consid-

⁶⁰ (a) Groggins, *op. cit.*, 4th ed., p. 538; (b) *ibid.*, p. 550; (c) *ibid.*, p. 539; (d) *ibid.*, pp. 495, 532.

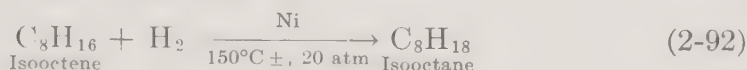
⁶¹ (a) Kirk and Othmer, *op. cit.*, vol. 2, p. 678; (b) *ibid.*, vol. 7, p. 701; (c) *ibid.*, vol. 4, p. 763; (d) *ibid.*, vol. 1, p. 319; (e) *ibid.*, vol. 1, p. 312, vol. 3, p. 182; (f) *ibid.*, vol. 1, p. 331.

⁶² R. N. Shreve, "The Chemical Process Industries," 2d ed., McGraw-Hill Book Company, Inc., New York, 1956. See Coal Chemicals chapter for flow sheet, conditions, and products.

erably. The reaction is a hydrogenolysis. Methanol is used as the solvent.



Isooctane. For high-octane motor fuel,

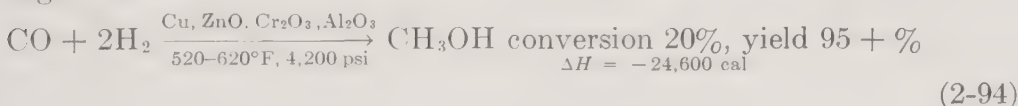


Lauryl Alcohol from Coconut Oil (or Fatty Acid Therefrom).

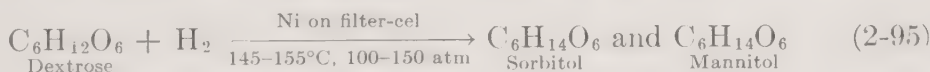


The coconut oil is about half glyceryl trilaurate, with about 17 per cent myristic ester and minor amounts of others.

Methanol. This has become one of our cheapest organic compounds and is used as a solvent and as a raw material. A flow sheet is shown in Fig. 2-4.^{60d, 61e}



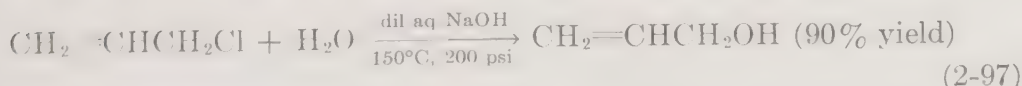
Sorbitol from Dextrose (Glucose). The process competes with the electrolytic reduction and gives yields about 95 per cent.^{61f}



Toluene and Benzene by Hydroforming, etc. This is a dehydrogenation and is one of the principal reactions of the widely used "platforming" in the petroleum industry to furnish aromatics and high-octane gasoline. A typical reaction is



2-8. Hydrolysis. *Allyl Alcohol from Allyl Chloride.*^{63a}



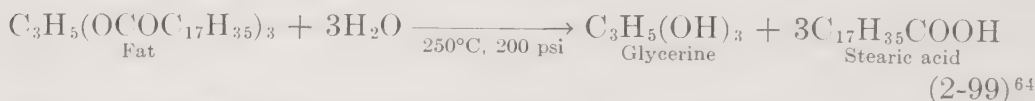
⁶² (a) Kirk and Othmer, *op. cit.*, vol. 7, p. 751; (b) *ibid.*, vol. 1, pp. 279, 285; (c) *ibid.*, vol. 6, pp. 232; (d) *ibid.*, vol. 7, p. 748.

Ethyl Alcohol from "Ethyl Sulfate." See Fig. 2-2 and Ethyl Hydrogen Sulfate and Diethyl Sulfate.



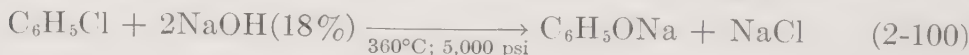
Some ether is formed. The pressures are somewhat lower than the range of 100 to 500 psi used for the esterification. Ethyl alcohol is also obtained^{63b} from ethylene and water over a complex catalyst of iron, nickel, or cadmium phosphate, but with low (5 to 20 per cent) conversions, using temperatures around 300°C and pressures from 300 to 1,200 psi.

Glycerine and Fatty Acids. While the saponification of fats to give soaps is not a pressure reaction, it is necessary to use pressure when splitting fats with water to keep the hydrolysis water in the liquid phase at the temperature needed to secure a practical reaction rate. The following is a typical reaction.

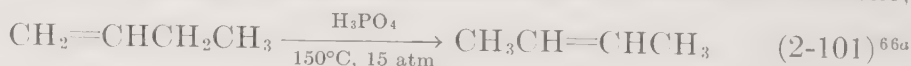


The yield is 98 per cent, and a relatively strong (15 per cent) glycerine solution results. This hydrolysis is carried on continuously and in a countercurrent manner in a vertical tower.^{63c, 65a}

Phenol from Chlorobenzene. These are depicted in Fig. 2-5.^{63d, 65b}



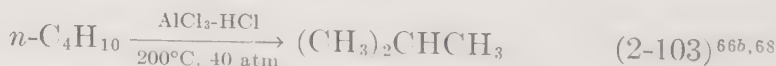
2-9. Isomerization. *Butene.* Phosphoric acid and diatomaceous earth serve as the catalyst in the isomerization of 1-butene to 2-butene,



Diisopropyl. The isomate process yields pentanes and hexanes with higher octane numbers than the starting materials,



Isobutane. This is a liquid-phase reaction using Friedel-Crafts-type catalyst.



⁶⁴ R. N. Shreve, "The Chemical Process Industries," 2d ed., chap. 29, McGraw-Hill Book Company, Inc., New York, 1956.

⁶⁵ (a) Groggins, *op. cit.*, 4th ed., p. 675; (b) *ibid.*, 4th ed., pp. 660, 695-701.

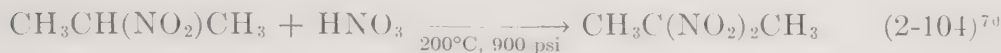
⁶⁶ (a) Groggins, *op. cit.*, 3d ed., p. 751; (b) *ibid.*, 4th ed., p. 894.

⁶⁷ J. E. Swearingen, R. D. Geckler, and C. W. Nysewander, *Trans. Am. Inst. Chem. Engrs.*, **42**:573 (1946).

⁶⁸ V. Ipatieff and H. Pines, U.S. patent 2,169,494 (1939); British patent 498,463 (1938).

Butane may also be isomerized⁶⁹ at 90 to 105° and 250 to 350 psi in the presence of aluminum chloride and aluminum bromide.

2-10. Nitration. *2,2-Dinitropropane.* A continuous-pipe reactor provides a per-pass conversion of about 10 per cent,



Ferrous reactor surfaces promote oxidation, but chrome-nickel steel may be used if mixed sodium and potassium nitrates are sprayed continuously into the reactor. Materials which apparently do not interfere with the reaction are glass, silica, platinum, and gold. This generalization, as well as the reaction conditions specified, applies to dinitration of three- to five-carbon nitroparaffins whose original nitro group is not attached to a primary carbon atom.

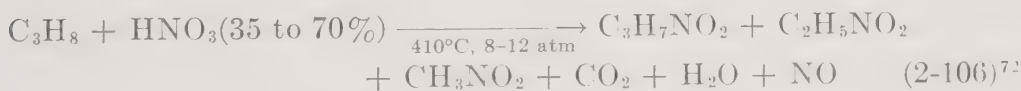
Nitroethane. This is a by-product of the nitration of propane.

Nitromethane. The reaction takes place in Pyrex-glass or chrome-nickel-steel reactors at pressures up to 1,000 psi. Mostly supplied as a by-product of nitration of propane.



The nitration becomes more difficult to control as pressure is increased, and oxidation catalysts deposited on the reaction tubes may result in lowered conversion.

Nitropropanes. This equation is typical for the nitration of paraffins, an important class of reactions, which have been commercialized for propane.



Both 1-nitro- and 2-nitropropane are obtained. Yields of nitro compounds are low, and conversions are lower, with oxidation products always present; elevated pressures increase the reaction rate and the difficulty of temperature control; most catalysts accelerate oxidation rather than nitration. The reaction is highly exothermic, and a large excess of propane is employed to help control the reaction temperature and thus to lessen the oxidation products.

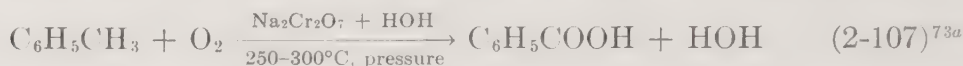
⁶⁹ Kirk and Othmer, *op. cit.*, vol. 7, p. 618.

⁷⁰ W. I. Denton, et al., U.S. patent 2,425,467.

⁷¹ H. B. Hass, H. Schlechter, L. G. Alexander, and D. B. Hatcher, *Ind. Eng. Chem.*, **39**:919-924 (1947).

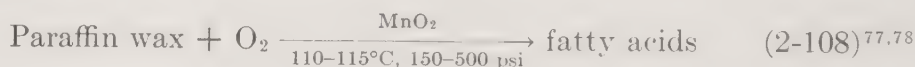
⁷² H. B. Hass and H. Schlechter, *Ind. Eng. Chem.*, **39**:817-21 (1947).

2-11. Oxidation. Benzoic Acid. Air blown into the reactor serves to regenerate the dichromate oxidizing agent in the liquid-phase oxidation.



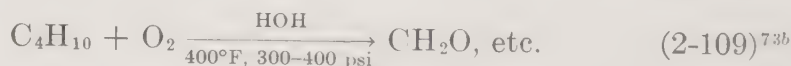
Toluene may also be oxidized to benzoic acid in 6 to 7 hr in the liquid phase by nitric acid in the presence of manganese dioxide at 80 to 90°C and under 35 to 40 psi. At 185 to 200°C and 50 atm toluene may be converted directly by air in the presence of cobalt or manganese acetates or methyl ethyl ketone. Alkylated aromatics may be oxidized in the side chain in noncatalytic liquid-phase reactions using air under pressure.⁷⁴ At atmospheric pressure benzoic acid is formed from ethylbenzene;⁷⁵ at 50 atm and 210°C *benzyl alcohol* may be obtained along with nuclear oxidation products.⁷⁶

Fatty Acids. Mixtures of petroleum hydrocarbons react continuously in an 8-hr cycle in the liquid phase in the presence of dissolved or solid catalysts.



Salts of manganese, copper, iron, chromium, and vanadium may be used as soluble catalysts.

Formaldehyde. This reaction is general for low-molecular-weight hydrocarbons and provides a variety of oxygenated products ranging from butanol through various degraded products. In this case butane is mixed with compressed air and steam and then is quenched with water after reaction.



Bludworth advocates reaction with steam as a diluent also, recommending 1 part butane by weight per 5 parts air. At 20 to 30 atm and 750°F, 34 parts steam are used and the reaction takes 1.15 sec; at 3.5 to 20 atm and 550°F, 18.5 parts steam are used and the reaction takes 0.3 sec.⁷⁹ At 8 atm and 335–350°F, cracked gas was oxidized with 3 to 5 per cent oxygen; the cold-flame oxidation resulted in a maximum yield under these

⁷³ Kirk and Othmer, *op. cit.*, vol. 2, pp. 464–465; (b) *ibid.*, vol. 6, p. 868; (c) *ibid.*, vol. 1, p. 312; (d) *ibid.*, vol. 9, pp. 333–335, 418.

⁷⁴ H. O. Forrest and P. K. Frolich, U.S. patents 1,902,550, 1,936,427 (1933).

⁷⁵ E. B. Maxted, *J. Soc. Chem. Ind. (London)*, **47**:101–105T (1928).

⁷⁶ D. M. Newitt and P. Szego, *J. Soc. Chem. Ind. (London)*, **52**:645 (1933).

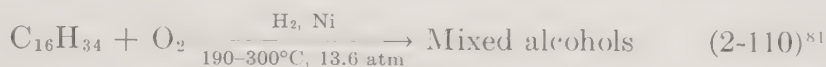
⁷⁷ M. Luther and K. Goetze, U.S. patents 2,015,347 (1936); 2,095,338 (1937).

⁷⁸ E. Keunecke, U.S. patent 2,095,473 (1937).

⁷⁹ J. E. Bludworth, U.S. patents 2,128,908, 2,128,909 (1938); 2,369,710 (1944).

conditions of 12 to 15 per cent formaldehyde and a like amount of higher aldehydes.⁸⁰

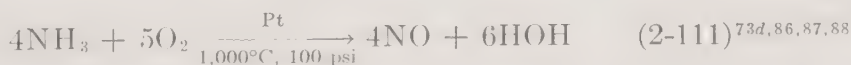
Hexadecane, Oxidation of. A narrow, glass-lined reaction tube served to confine the mole mixture of 0.5 moles oxygen per mole of hexadecane.



Conversions of 17 per cent were obtained for the two-step process which yielded alcohols having molecular weights as high as 165.

Hydrocarbons, Oxidation of. Pressure oxidation of hydrocarbons yields various products depending on raw materials and conditions used. Wiezevich has investigated the vapor-phase oxidation of various saturated hydrocarbons with air and in the absence of a catalyst with respect to temperature, pressure, concentration, contact time, and recirculation.⁸² Newitt has shown that pressure accelerates the rate of reaction, exerts a directive influence on the primary oxidation process, and partly determines the distribution of oxygen atoms in the products of combustion of aliphatic and aromatic hydrocarbons.⁸³ Temperatures of 100 to 300°C, pressures of 15 to 50 atm, and short time of contact are usual conditions for production of alcohols and carbonyl compounds from saturated hydrocarbons.^{73c} Low oxygen-to-hydrocarbon ratios (0.05 to 0.15) are used with pressures from 50 to 250 atm, temperatures from 200 to 600°C, short contact time, and a variety of catalysts; conditions are most extreme for the lowest members of the hydrocarbon series.⁸⁴ Diluents such as steam have been used commercially, as have water quenches.⁸⁵

Nitric Acid. Increasing pressure increases effective catalyst life, temperature at which the maximum yield is obtained, and concentration of resulting nitric acid, but it also increases the cost of stainless-steel absorption towers. One hundred pounds per square inch is an over-all good compromise figure.



⁸⁰ B. V. Aivazov and B. I. Gnyubkin, *J. Appl. Chem. (U.S.S.R.)*, **13**:869-878 (1940).

⁸¹ H. B. Hass, E. T. McBee, and J. W. Churchill, *Ind. Eng. Chem.*, **37**:445 (1945).

⁸² P. J. Wiezevich and P. K. Frolich, *Ind. Eng. Chem.*, **26**:267-276 (1934).

⁸³ D. M. Newitt, *Chem. Revs.*, **21**:299-317 (1937).

⁸⁴ D. M. Newitt and A. E. Haffner, *Proc. Roy. Soc. (London)*, **134A**:591-604 (1932).

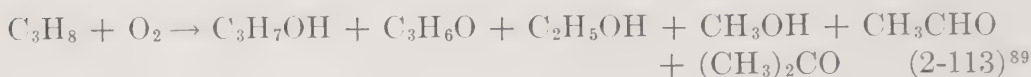
⁸⁵ J. E. Bludworth, U.S. patents 2,128,908, 2,128,909 (1938); 2,369,710 (1944).

⁸⁶ V. I. Atroschenko, *J. Appl. Chem. (U.S.S.R.)*, **19**:1214-1224 (1946).

⁸⁷ Ullmann, *op. cit.*, 2d ed., **9**:18-22.

⁸⁸ Shreve, *op. cit.*

Propane, Oxidation of. High pressures produce oxidation of the β atom. The products are alcohols and carbon oxides with some aldehydes, acetone, and acids, with no hydrocarbons. Using a 1:5 ratio of propane to air at 30 atm with increase in temperature from 260 to 286°C, the ratio of alcohols and aldehydes to acetone and isopropyl alcohol falls from 13 to 5 and the ratio of carbon monoxide to carbon dioxide increases from 0.4 to 2.5.



Using a 1:3.6 ratio of propane to air at 1 to 100 atm and at temperatures from 373 to 250°C, the first-mentioned ratio above falls from 22 to 1.2 and the second drops from 2.9 to 0.4; the ratio of *n*-propanol to methanol and ethanol increases. Oxidation of propanol at 56 atm and 240°C yields acetic acid, ethanol, propionaldehyde, ethane, and propionic acid.

Butane, Oxidation of. See Fig. 2-1.

2-12. Polymerization. A number of publications have dealt with polymerizations carried out under pressure. Peroxides are essential for polymerization of aliphatic aldehydes and isoprene under high pressure.⁹⁰ The polymer of butyraldehyde is said to be similar to that of formaldehyde, but is stable only at high pressure.⁹¹ Eighteen tables give data on a large number of reactions.⁹² Rate of polymerization of styrene increased tenfold at 3,000 atm.⁹³ The energy of activation of the polymerization was greater at lower temperatures.⁹⁴ The degree of polymerization of styrene is independent of pressure.⁹⁴ Effects of temperature, pressure, steam concentration, and contact time on polymerization of 2-butene in a continuous apparatus are given.⁹⁵ Polymerization of butanol (and of butene from the side reaction of dehydration) increases with pressure.⁹⁶ Butadiene may be polymerized in the liquid phase under high pressure in the presence of fluorides at 100°C to form a rubberlike polymer containing one ring per four butadiene molecules; at 125°C three out of four molecules cyclized; at 150°C only cyclic polymers were

⁸⁹ D. M. Newitt and W. Schmidt, *J. Chem. Soc.*, **1937**:1665-1669.

⁹⁰ J. B. Conant and W. D. Peterson, *J. ACS*, **54**:629-634 (1932).

⁹¹ J. B. Conant and E. D. Tongberg, *J. ACS*, **52**:1659-1669 (1930).

⁹² A. I. Dintses, B. A. Korndorf, S. S. Lochinov, and S. L. Lelechuk, *Uspekhi Khim.*, **7**:1173-1230 (1938).

⁹³ R. E. Gillham, *Trans. Faraday Soc.*, **46**:497-503 (1950).

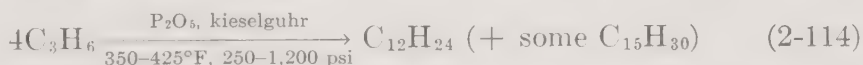
⁹⁴ P. P. Kobeko, E. V. Kuvshinskii, and A. S. Semenova, *Zhur. Fiz. Khim.*, **24**:345-352 (1950).

⁹⁵ L. F. Marek and R. K. Flege, *Ind. Eng. Chem.*, **24**:1428-1431 (1932).

⁹⁶ C. M. Sliepcevich and G. G. Brown, *Chem. Eng. Progr.*, **46**:556-562 (1950).

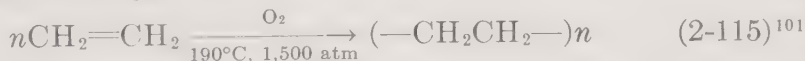
formed, but this polymer was a viscous liquid.⁹⁷ A large number of unsaturated organic compounds containing conjugated double bonds are polymerized at 2,000 to 9,000 atm and 20 to 74°C, giving first-order rate constants with an energy of activation of about 20,000 cal; at about 6,000 atm a pressure increase of 1,000 atm doubles the rate. The latter is also increased by substituent groups in the β position in the order alkyl, phenyl, chloride, bromide, iodide; in the α position halogen groups are less effective and alkyl groups are inhibitory.⁹⁸ With increasing pressure the temperature at which polymerization begins decreases; data on the influence of pressure on polymerization velocity constants of styrene, isoprene, vinyl acetate, dimethyl butylene, and indene, are given, and pressure influences the polymerization of these materials to a greater extent than it does most materials.⁹⁹ Methyl methacrylate can be polymerized under pressure in the presence of air.¹⁰⁰ The greater the pressure, the higher the rate of polymerization and the molecular weight. Another catalyst is hydroquinone.

Tetramer. A flow sheet for the following reaction is given in Fig. 2-8.



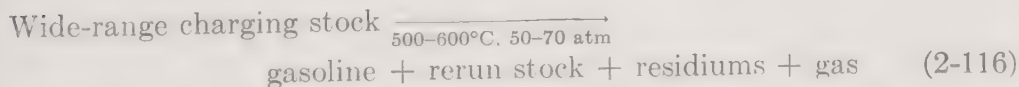
This is employed in alkylating benzene to furnish dodecylbenzene for detergents.

Polyethylene. Oxygen (less than 0.1 per cent) catalyzes the highly exothermic reaction which takes place in high-pressure autoclaves. A flow sheet is given in Fig. 2-7.



The reaction has also been carried on successfully in the liquid phase by the emulsion method at 300 atm and 200°C.

2-13. Pyrolysis. *Cracking Petroleum.* The thermal pressure cracking of petroleum fractions is one of the oldest of processes for furnishing cracked gasoline, dating from just before World War I. A modern version is presented in Fig. 2-9.



⁹⁷ Y. M. Slobodkin and F. V. Rachinskii, *Doklady Akad. Nauk S.S.S.R.*, **58**:69 71 (1947).

⁹⁸ H. W. Starkweather, *J. ACS*, **56**:1870-1874 (1934).

⁹⁹ G. Tammann and A. Pape, *Z. anorg. Chem.*, **200**:113-132 (1931).

¹⁰⁰ L. F. Vereschchagin, V. Derevitskaya, and Z. A. Rogovin, *J. Phys. Chem. (U.S.S.R.)*, **21**:233 240 (1947).

¹⁰¹ Groggins, *op. cit.*, 4th ed., pp. 775-776.

2-14. Flow Sheets. Ten flow sheets¹⁰²⁻¹⁰⁵ have been selected to illustrate the pressure processes that have been listed and described under the appropriate unit process in the preceding sections. These flow sheets are arranged alphabetically as Figs. 2-1 to 2-10 with a short description of each process.

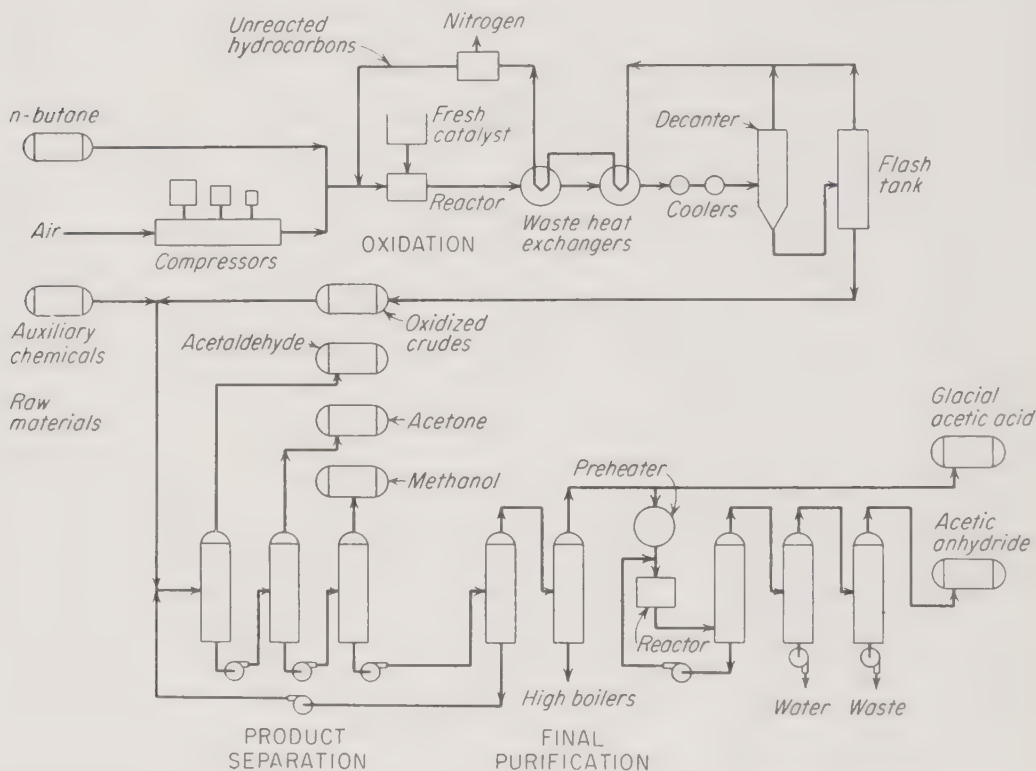


FIG. 2-1. Flow sheet for butane oxidation according to the Pampa plant of the Celanese Corporation of America. (*Petroleum Refiner*.) After experience with propane and butane oxidation at Bishop, Texas, the Pampa, Texas, butane oxidation was started in 1952. The charge is primarily normal butane with acetic acid and acetic anhydride the principal products.¹⁰²

¹⁰² "Process Handbook," The Gulf Publishing Company, Houston, 1953; or *Petroleum Refiner*, **32**(11):146 (1953).

¹⁰³ *Ibid.*, **32**(11):126 (1953).

¹⁰⁴ Shreve, *op. cit.*, chaps. 31, 37.

¹⁰⁵ "Process Handbook," The Gulf Publishing Company, Houston, 1953; or *Petroleum Refiner*, **32**(11):122 (1953).

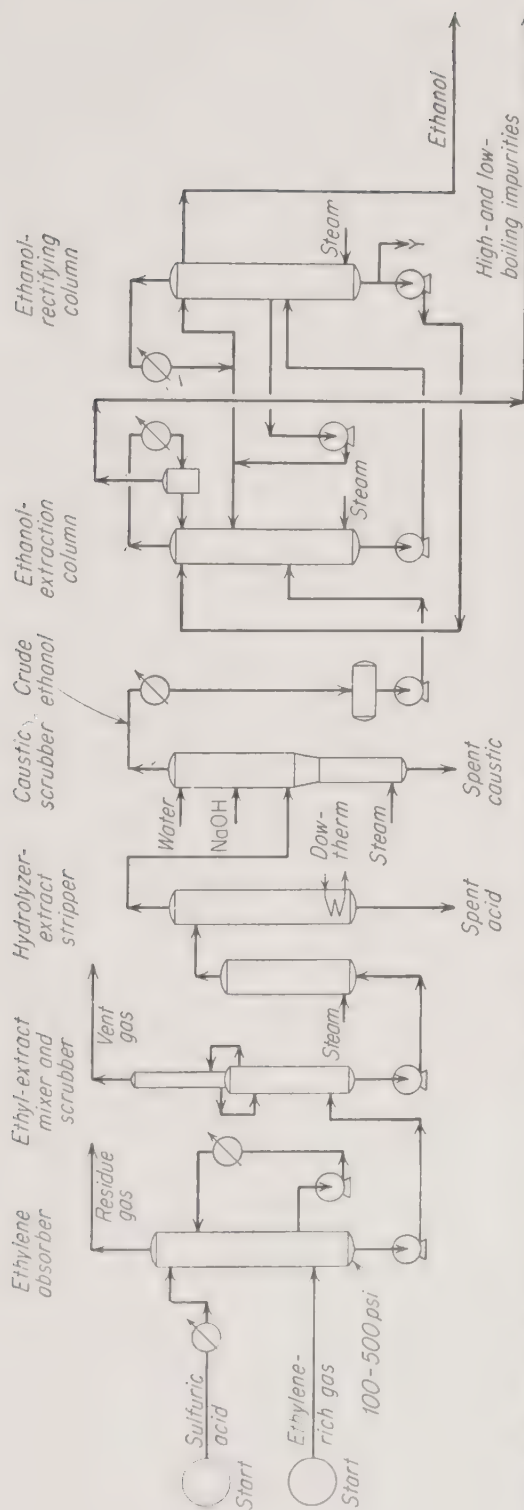


FIG. 2-2. Flow sheet for manufacture of ethyl alcohol through "ethyl sulfate." (*Petroleum Refiner*.) Over half of all the ethyl alcohol consumed in the United States is made from ethylene. Usually the ethylene-rich gas (35 to 95 per cent C_2H_4) is esterified with 98 per cent sulfuric acid under pressures from 100 to 500 psi at a temperature of 130 to 170°F with the exothermic heat removed by cooling coils and with waste gases vented. Hydrolysis takes place upon addition of a measured amount of water at a pressure somewhat lower than that used for the esterification. Residence times are as long as 3 hr at temperatures as high as 250°F, using live steam. Rectification is employed for the ethyl alcohol. Some ether is always formed, but conditions are usually chosen to minimize ether formation. Any excess ether can be hydrated to ethyl alcohol by water vapor over a suitable catalyst.^{103,104} The diluted sulfuric acid is strengthened and reused.

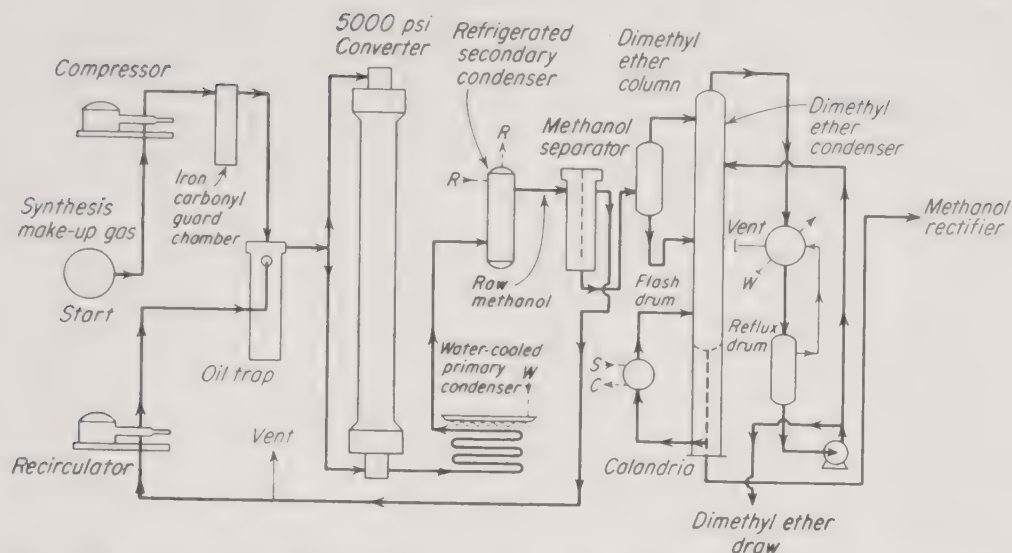
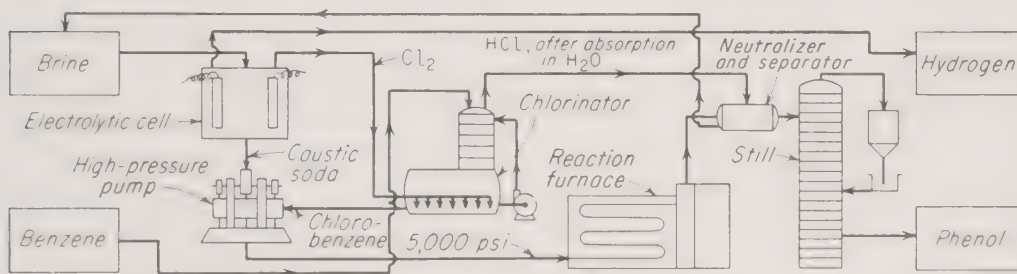


FIG. 2-4. Flow sheet for methanol. (*Petroleum Refiner.*) The highly exothermic hydrogenation of carbon monoxide to methanol is one of the large-scale processes of the United States. The compressed carbon monoxide and hydrogen pass through a heat exchanger counter to reaction products in the converter. About 20 per cent conversion takes place with the methanol condensed and removed. The unconverted gases have a small percentage vented to keep inerts (methane, nitrogen, and argon) low. These gases are recompressed by the recirculator pump and mixed with make-up gas, and passed on to the converter. The crude methanol is rectified.¹⁰⁵



Note: Small quantities of copper and sodium oleate are used as catalysts

Caustic soda	120 lb	} To produce 100 lb phenol and some diphenyl oxide*
Chlorobenzene	132 lb	

*If no D.P.O. is desired, add 0.1 mole with reactants

FIG. 2-5. Phenol flow sheet—chlorobenzene process. (*After Shreve, Chemical Process Industries.*) Chlorobenzene and 18 per cent sodium hydroxide are heated to reaction temperature (360°C) in a double-pipe heat exchanger counter to the reaction product (not shown in flow sheet). The raw materials, with their mutual solubility enhanced at this temperature and pressure (to maintain a single liquid phase), are pumped continuously through a pipe autoclave to form sodium phenate. This latter is neutralized with hydrochloric acid. The phenol is separated and distilled. One-tenth mole of diphenyl oxide is formed, and it can either be removed for sale or recirculated to lessen formation of further amounts.

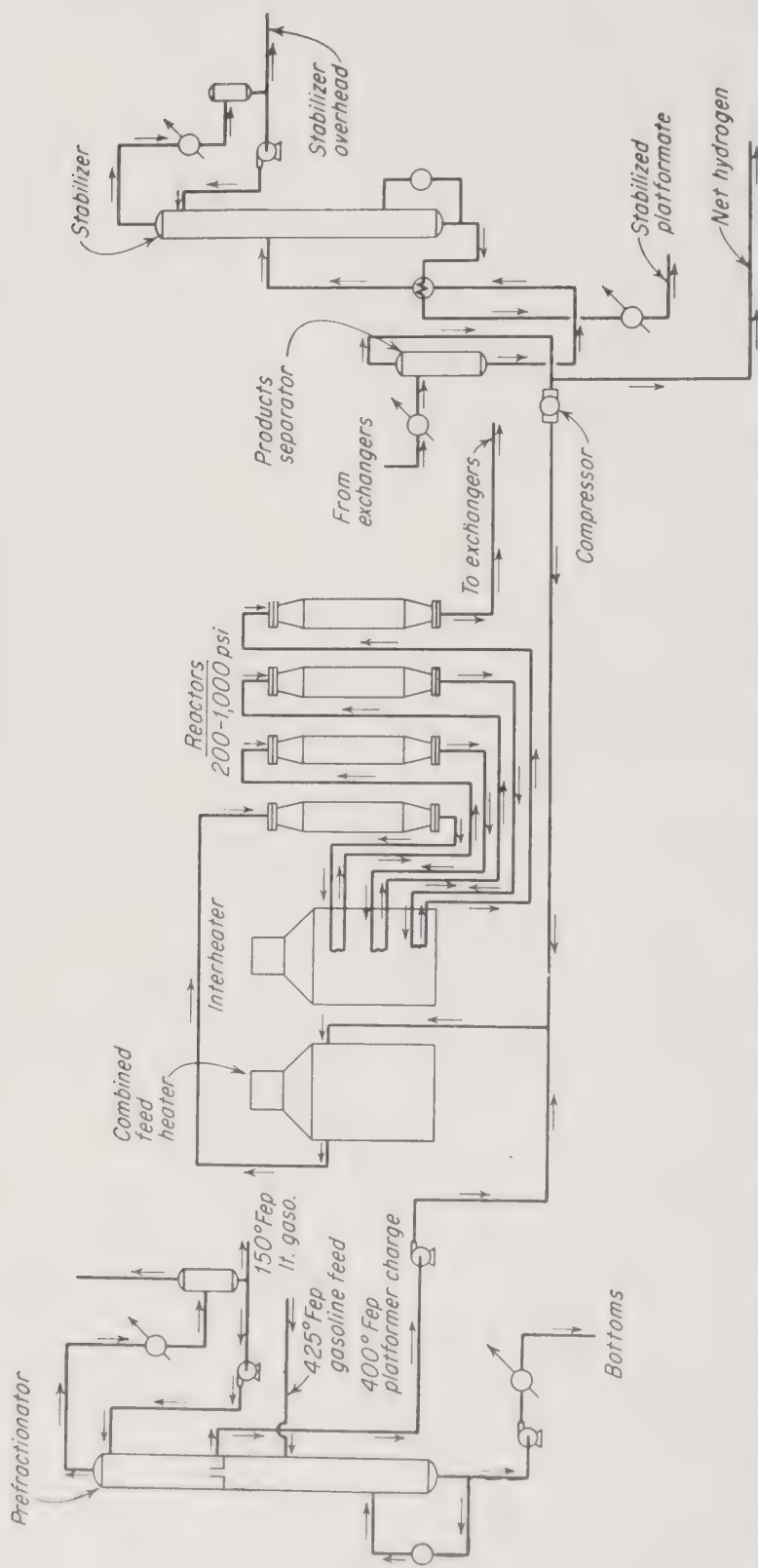


FIG. 2-6. Platforming flow sheet. (*Universal Oil Products Company.*) This "platforming" or hydroforming process upgrades by reforming in the presence of hydrogen and a platinum catalyst many different gasoline fractions, producing larger quantities of benzene, toluene, and xylenes, and upgrading the octane number of gasolines. "In operation, the gasoline vapors, mixed with recycle hydrogen, are passed through a series of reactors, containing the catalyst, at 850 to 950°F and 200 to 1,000 psi. Hydrogen of about 90 per cent purity is separated from the reactor effluent, and the platformate is stabilized to obtain high-octane gasoline, from which aromatics can be separated if desired."

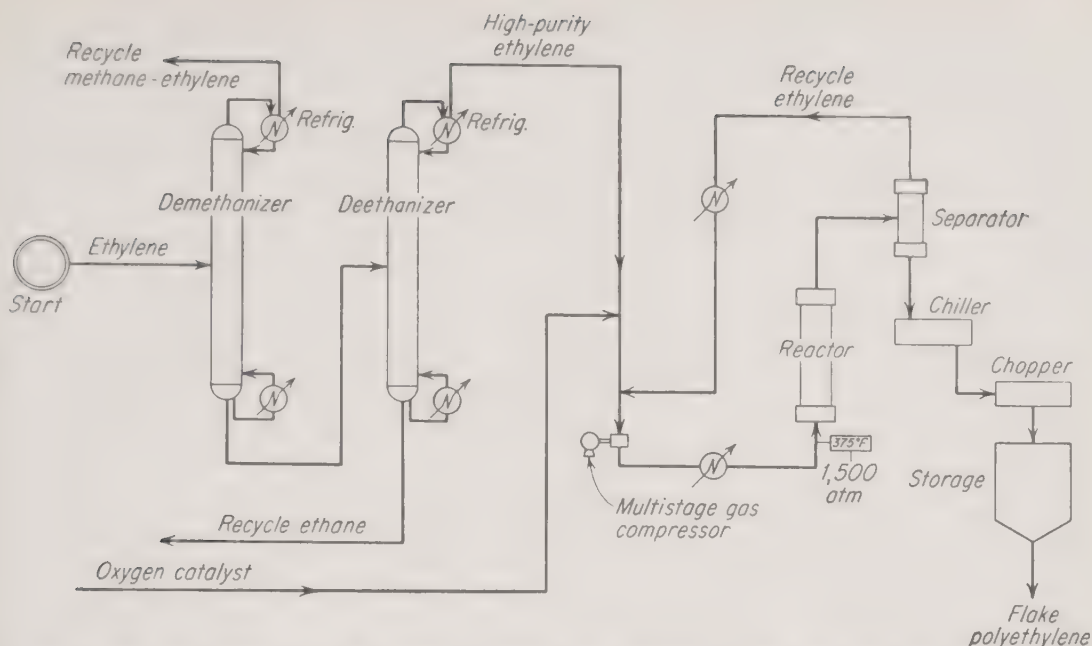


FIG. 2-7. Polyethylene flow sheet. (Petroleum Refiner.) As the ethylene must be of a minimum purity of 99.8 to 99.9 per cent, the ordinary 95 per cent ethylene is upgraded under pressure of 400 to 500 psi as shown in this flow sheet. A small quantity of oxygen (600 ppm) is added as a catalyst, and the mixture is compressed to 1,500 atm. The mixture is heated to 375°F and conducted through the stainless-steel reactor. The reaction is slow, and the temperature of 375°F must be maintained. At the separator, unreacted ethylene is removed and may be recycled. The liquid from the separator solidifies at around 230°F.

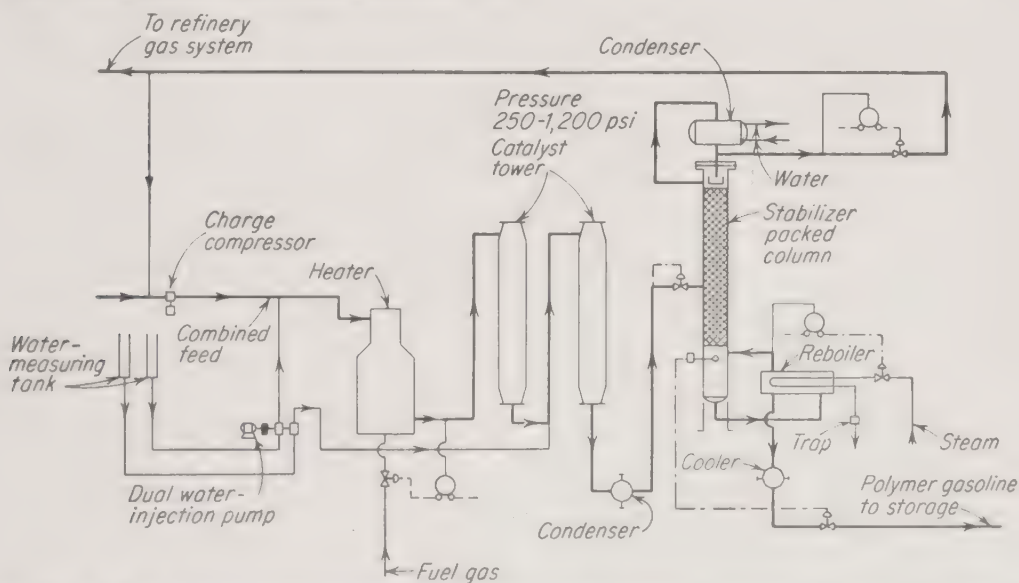


FIG. 2-8. Flow sheet for catalytic polymerization process—chamber type. (Universal Oil Products Company.) Tetramer ($C_{12}H_{24}$) for dodecylbenzene for detergents is made by polymerizing propylene under pressure and at controlled temperature. The propylene and/or butylenes can also be polymerized to high-grade motor or aviation gasoline. The polymerization process is carried on using a catalyst, usually of the solid phosphoric acid type (P_2O_5) on kieselguhr activated with a certain amount of water). This catalyst is kept at temperatures from 350 to 425°F and at pressures from 250 to 1,200 psi. The heat of the polymerization process is kept at the necessary point by injection of recycling light hydrocarbons low in olefins to the reactor inlets and between the catalyst beds in the catalyst towers as a "quench."

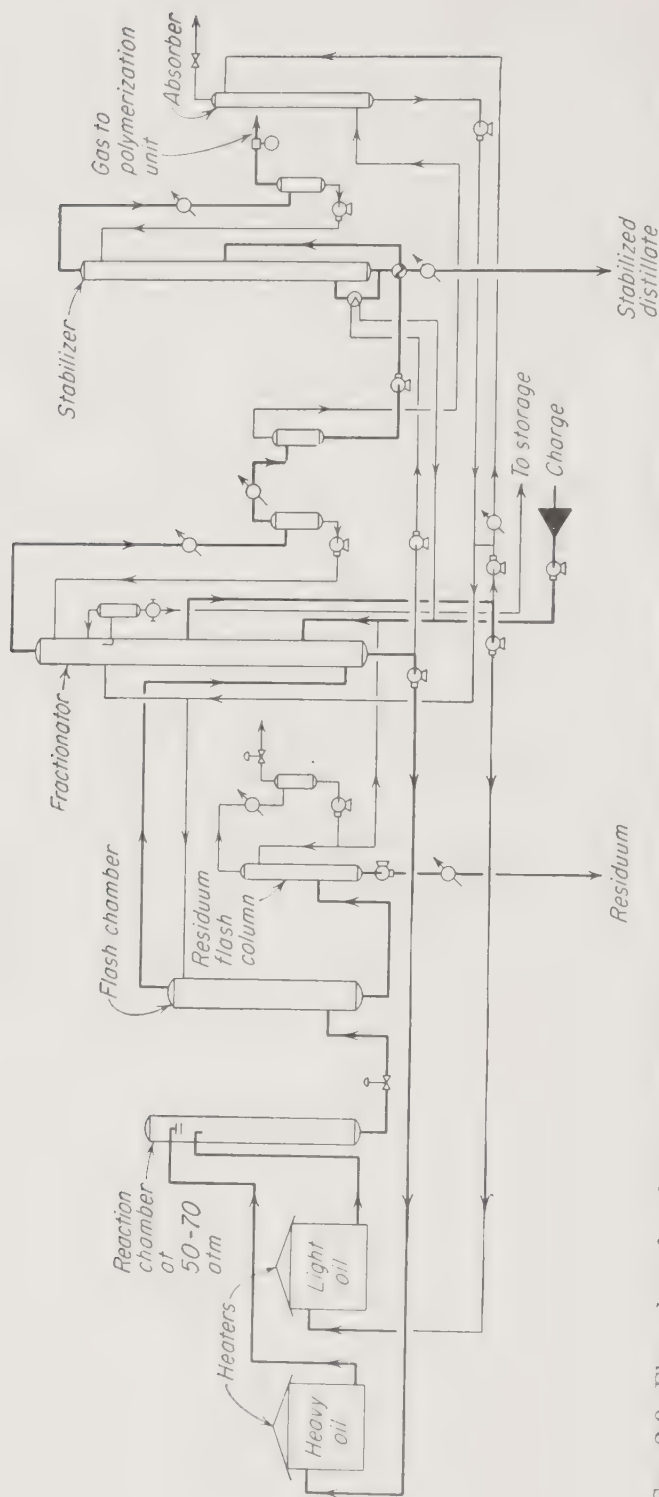


FIG. 2-9. Flow sheet for thermal cracking by the two-coil selective process. (*Universal Oil Products Company*.) The raw materials may be heavy reduced crudes, pitch, virgin-gas oil, cycle oils, tank bottoms, and naphtha. This pyrolysis, or cracking, is usually carried out at 500 to 600°C and under 50 to 70 atm pressure. The use of the two-coil heating system enables selective temperatures best suited to the heavy- and the light-oil charging stocks to be used. Note that transfer lines from the two heaters enter the top of the downflow reaction or cracking chamber. The products pass through a pressure-control valve to the flash chamber, fractionator, and stabilizer. The product is a stabilized gasoline.

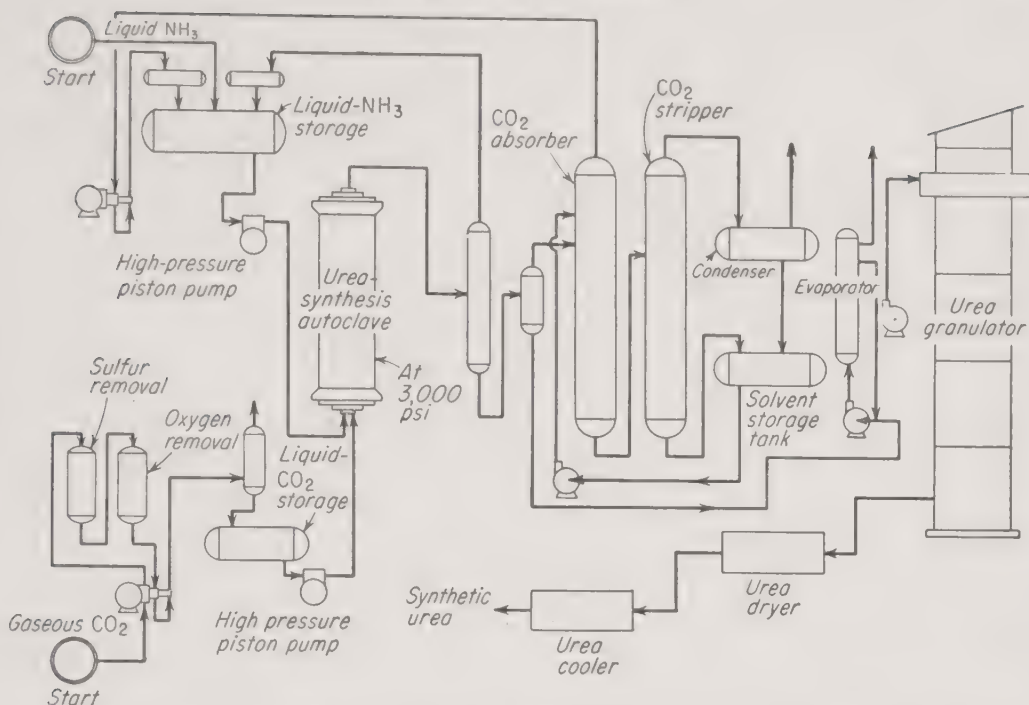


FIG. 2-10. Flow sheet for granular urea from liquid ammonia and gaseous carbon dioxide. (*Petroleum Refiner.*) Using a 6:1 molal ratio of ammonia to carbon dioxide, at 175°C and 3,000 psi, the conversion of the ammonium carbamate is about 76 per cent. The stream flowing from the autoclave consists of urea, water, ammonium carbamate, and ammonia. Pressure is partly lowered, permitting the excess (4 moles) of ammonia to be removed and condensed as liquid ammonia to be recycled. After another pressure reduction, the product enters the ammonium carbamate decomposer, and carbon dioxide is removed from the overhead stream from this by absorption in a solvent, permitting the remaining ammonia to be compressed, liquefied, and returned to the system. The aqueous urea solution is concentrated to 95 per cent urea in water and pumped to the granulator.

CHAPTER 3

METALS

H. C. VAN NESS

A brief introduction to some of the factors to be considered when selecting metals for use in constructing high-pressure equipment is given in this chapter.¹ The proper choice of materials is important, for service failures of high-pressure equipment can be both expensive and dangerous. There are many metals and alloys available, together with data on their properties. Properly used, such data permit the engineer to make intelligent selections of metals for diverse applications.

For applications where high strength is an important factor, one naturally thinks of steel as the most economical material of construction, and quite rightly so. In fact, it seems safe to say that when steel is not to be used, there must be some special reason. Thus, this discussion will be concerned mainly with steels, though mention will be made of a number of special alloys.

There are certain fundamentals which are basic to an understanding of the behavior of metals, and these are considered in some detail. The reader whose needs go beyond this must have recourse to more comprehensive treatments which are available in any number of texts and reference books, some of which are listed in footnotes in this chapter.

3-1. The Common Mechanical Tests. The mechanical properties of metals at room temperature are measured by a number of conventional tests.^{2,3} The most common of these are hardness and tensile tests. In addition, impact and fatigue tests are of value for some applications. While there are others, only these four will be discussed. It cannot be overemphasized that these tests show only how a metal behaves under certain specific test conditions—conditions which exist only rarely in actual service. Thus, the engineer must be careful not to suppose that the successful design of equipment rests solely on the results of conven-

¹ For table of symbols see nomenclature at end of Chap. 6.

² "Metals Handbook," 1943 ed., pp. 85-140, American Society for Metals, Cleveland, Ohio, 1943.

³ "The Making, Shaping and Treating of Steel," 6th ed., pp. 1354-1427, United States Steel Company, Pittsburgh, 1951.

tional tests, however quantitative they may be. Resort must be had to "engineering judgment," experience, and in some instances to actual service tests. Above all, the successful use of the results of conventional mechanical tests depends upon proper design and manufacture.

Hardness Tests. The most common mechanical test is the hardness test, and there are a number of these. The ones usually used in the United States are the Brinell and Rockwell tests. Both are conveniently made with the aid of hand-operated machines which cause a small indenter of specified size and shape (ball, cone, or pyramid) to be forced under a specified load into the sample of the metal to be tested. The results of such tests are read from arbitrary scales which indicate the difficulty of indenting the metal. Different tests use different scales which are not, in general, related in any simple way. However, the two scales most often used for steels—the Rockwell C scale and the Brinell hardness number—differ roughly by a factor of 10, Rockwell C values ranging from 20 to 60 and Brinell hardness numbers from about 200 to 600, the higher numbers indicating greater hardness.

The numerical values obtained by hardness tests are meaningless in themselves. Their value lies in the fact that they are a guide to tensile properties, which are considerably more trouble to measure. This approximate relationship for hardened and tempered steels is shown in Fig. 3-8.

The Tensile Test. Since the tensile properties of metals are the most commonly used properties in design, the tensile test deserves to be considered at some length. In such tests a specimen of standard size and shape (there are several standards) is stretched in a machine until it breaks. As the load is applied, the stretch of the specimen within a certain gauge length is measured and recorded as a function of load. From these data, the conventional stress-strain diagram can be determined. Such a diagram is shown in Fig. 3-1. Stress σ is here defined as load per unit of original cross-sectional area, usually in pounds per square inch, and strain ϵ as elongation of the gauge length per unit of original gauge length, usually in inches per inch. Thus the conventional stress-strain diagram shows neither true stress nor true strain, for in constructing it one ignores the reduction in cross-sectional area and the elongation of the gauge length as the specimen is stretched. The departure of the true stress-strain curve from the conventional one is indicated in Fig. 3-1.

With reference to Fig. 3-1, let us define a number of common terms. Point *A* is known as the proportional limit. It is the limiting stress at which Hooke's law is valid. This law expresses the direct proportionality which exists between stress and strain up to this limit and is written $\sigma = E\epsilon$, where σ and ϵ are stress and strain, respectively, as previously

defined, and E is the proportionality constant, or modulus of elasticity. E is obviously equal to the slope of the stress-strain curve between the origin and point A . It is usually given in the units of pounds per square inch and has a value of about 30,000,000 for steel. In this region the metal stretches elastically, i.e., it will return to its original length if the load is removed.

Another quantity, useful in pressure-vessel design, is known as Poisson's ratio. In the elastic region the unit deformation or strain in the direction perpendicular to the load is directly proportional to the strain

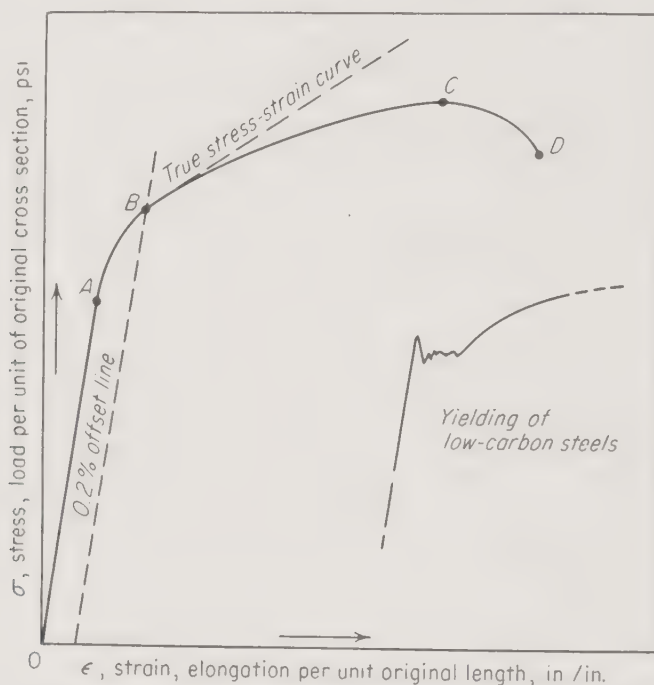


FIG. 3-1. Conventional stress-strain diagram for a ductile material.

in the direction of the load. Thus for a load applied in the y direction, $\epsilon_x = \nu \epsilon_y$, or $\nu = \epsilon_x / \epsilon_y$, where ν is called Poisson's ratio. It has a value of about 0.3 for steels. Since $\sigma_y = E \epsilon_y$, $\epsilon_x = \nu \sigma_y / E$.

The stress at point B is known as the yield strength and is defined quite arbitrarily as the stress at a particular elongation, which is determined as follows: Starting at a point on the strain ordinate corresponding to a given value, usually 0.002 in./in. (usually referred to as a strain of 0.2 per cent), a line is drawn parallel to the stress-strain curve in the proportional region and is extended to this curve to locate point B . This is called the "offset" method, and yield strengths reported in the literature are usually "0.2 per cent-offset" values. The term "yield point" is sometimes encountered and is properly applied only to metals such as low-carbon steels which stretch suddenly in the region between points A and B without any increase in load. Yielding of this kind is

shown at the right in Fig. 3-1. In such cases, the yield point is usually taken as the maximum on the stress-strain curve before the sudden yielding occurs.

The stress at point *C* is known as the ultimate tensile strength or sometimes simply as the tensile strength. In carrying out a tensile test, the load on the specimen is continuously increased up to point *C*, and the specimen continuously stretches; consequently its cross-sectional area continuously decreases. After the elastic limit is passed (somewhere between points *A* and *B*), this stretching represents inelastic, or irreversible or plastic, deformation and results in work-hardening, or a gain in strength of the metal. At point *C* this work-hardening exactly counteracts the decrease in area caused by stretching, since the load remains constant for at least a differential amount of stretching. Before point *C* is reached, the work-hardening effect overbalances the effect of area reduction, and the load carried by the specimen increases. After point *C* is passed, the area reduction occurs more rapidly than the work-hardening, and the specimen will continue to stretch until it fails, stretching so rapidly, in fact, that the load falls off from point *C* to point *D*, the point of fracture. This rapid stretching occurs because of a process called "necking," i.e., a rapid reduction of cross-sectional area confined to a short segment of the specimen. The true stress-strain curve rises continuously to the breaking point. However, this curve is rarely determined and is mentioned here only to emphasize the fact that the conventional diagram does not show true values of stress.

Not all metals when tested give the complete diagram as shown in Fig. 3-1, which is a diagram for a ductile material. Actually, failure may occur at any point on the curve from *A* onward. Very brittle materials undergo plastic yielding to only a slight extent and thus do not neck. In such cases, the curve shows no maximum, and the tensile strength is identical with the breaking strength. In any event, the tensile strength is the highest point on the curve, whether it be a maximum or the end of the curve.

The tensile test can be used to obtain information about the ductility of a metal as well as about its strength. Yield and tensile strengths, per cent elongation, and per cent reduction in area are ordinarily recorded as results from a tensile test. The latter two figures are qualitative indications of the ductility of the specimen, higher values indicating greater ductility. Per cent reduction in area is defined as the difference between the original cross-sectional area of the specimen and the minimum cross-sectional area of the broken specimen expressed as a percentage of the original area. Per cent elongation is defined as the increase in distance between marks indicating the gauge length, caused by breaking the specimen in tension, expressed as a percentage of the original gauge

length. Since the stretching of a specimen is not generally uniform throughout its gauge length (especially when necking occurs), the original gauge length should always be given, as, for example, by expressing results as per cent elongation in 2 in., etc.

The tensile test just described is the primary test used to evaluate the potentialities of a metal. However, it should be emphasized again that the particular results obtained are peculiar to the test, which is carried out on a standard specimen according to a standard procedure. In actual use, the metal may not come up to its potentialities for one reason or another. It may fail at a stress much lower than its ultimate tensile strength or even its yield strength if it is notched or grooved, if it is used in a corrosive atmosphere, or if it is flexed many thousands of times.

Impact Tests. Impact tests have often been regarded as measures of "toughness," but this word is so difficult to define that it might rather not be mentioned. Actually, these tests, and there are two common ones, the Charpy and the Izod, measure the energy required to fracture small standard notched bars with a single blow delivered in a particular manner. The results of such tests are very difficult to interpret and are in no sense design values. They may be useful in comparing metals having roughly the same tensile properties or in comparing different heat-treatments which give similar tensile properties to a given material. In general, high energy-absorption values are considered desirable, but the main function of these tests is to discriminate between metals of different susceptibilities to brittle fracture caused by the notch. Its importance lies in the fact that, in design, notches and other "stress raisers" are often unavoidable.

Impact tests are particularly valuable for steels which are to be used at low temperatures, for many steels become extremely brittle when the temperature is lowered below a certain value. This effect shows up first and most clearly in the impact tests. Thus, such tests are usually carried out over a range of temperatures. The temperature at which the impact values drop off rapidly is called the transition temperature. Metals which show such a transition are said to be temperature-sensitive, and care must be used in selecting them for low-temperature service. Many steels fall in this category, but values of the transition temperature range from room temperature down to very low values. Other materials, such as austenitic stainless steels, are not temperature sensitive. In fact, they may have higher impact values at -300°F than at room temperature. The selection of metals for use at low temperatures is discussed by Hoyt.⁴

Fatigue Tests. The tensile test gives yield-strength values which may be used for design under conditions of static loading. For fluctuating or

⁴ S. L. Hoyt, *Metal Progr.*, **55**:821 (1949).

cycling loads, these figures are not valid, being in general much too high. Thus, fatigue tests have been developed to measure the number of cycles (applications of load) metal specimens will stand without failure for various stresses. As the stress is lowered, the number of permissible cycles increases in a regular fashion until (at least for steels) a stress known as the endurance limit is reached. For stresses below this value, the metal will stand an infinite number of cycles. Fatigue failure is particularly dangerous because it usually occurs without warning and without plastic deformation of the metal, i.e., it occurs in a brittle fashion.

Again it must be emphasized that these tests are carried out under special conditions on special samples. Changing the conditions or the samples may change the results. In particular, the condition of the surface of the specimen is of major importance. The presence of grooves or scratches or rust or any other stress raiser may greatly reduce the endurance limit. Since fatigue tests are usually run on specimens with a mirror finish, the results of these tests must be used with a suitable factor of safety. Endurance limits for highly polished specimens of steel average about one-half the tensile strength. The effects of other surfaces and conditions are indicated by the approximate results for a hardened steel shown in Table 3-1. These results indicate how the brittle fracture of a steel having a tensile strength of 140,000 psi may occur at a stress only one-tenth that value.

TABLE 3-1†

	<i>Psi</i>
Tensile strength.....	140,000
Endurance limits:	
With mirror finish.....	70,000
With polish.....	62,000
With machining.....	55,000
With small-radius circular notch.....	42,000
With mill scale.....	25,000
Under water.....	21,000
Under salt water.....	14,000

† From G. T. Williams, "What Steel Shall I Use?" pp. 21-28, The American Society for Metals, Cleveland, Ohio, 1941.

3-2. The Structure of Metals. Ultimately, of course, metals are made up of atoms. In the solid state, these atoms are arranged in a space lattice with each atom more or less firmly bound to its neighbors, so that under ordinary circumstances it maintains its position. Furthermore, atoms are regularly arranged over large distances relative to their size. These domains of regularity are known as crystals or grains, and in the ideal case they are uniform throughout. Actually, minor disloca-

tions do exist within single crystals, but these do not alter the general orientation of the atoms.

For a given metal under given conditions, there is but one stable atomic arrangement, or lattice structure, but the stable arrangement may be different for different metals and may be different even for the same metal at different temperatures. Thus, the atoms of iron at room temperature are arranged in what is known as the body-centered cubic lattice structure, while at temperatures between about 900 and 1400°C, iron exists in the more compact face-centered cubic structure. The transformation between these two allotropic forms of iron plays a major role in the heat-treatment of steel. Magnesium, on the other hand, exists only in the close-packed hexagonal structure. The atomic structures of metals cannot be detected with the microscope, but become known only through crystallographic techniques such as X-ray-diffraction studies.

The crystal or grain structure of metals is evident from microscopic examination of a polished and etched sample. The process of preparing samples for microscopic examination is an art. The polishing must be carried to a point where the metal is given a mirror finish. Etching must be accomplished with a suitable etchant (usually an acid) which among other effects attacks the boundaries between grains preferentially.

If the material to be examined is not pure but contains more than one element, i.e., if it is an alloy, it may etch to show more than simple grain boundaries. However, this is not always the case, for some mixtures are solid solutions, i.e., they form a single, uniform phase which cannot be distinguished under the microscope from a pure metal. This case is illustrated in Fig. 3-2, which is a photomicrograph of a solid solution of iron and nickel in which the grain boundaries appear as irregular lines. On the other hand, many mixtures of metals form more than one phase; they are soluble in one another to only a limited extent, and these different phases usually etch differently so that grains of one phase may be distinguished from grains of the other under the microscope by their form or shade. Examples are shown in the next section in Figs. 3-4 and 3-5.

3-3. Iron and Steel. Pure iron is a rather soft and ductile material. Moreover, it is very difficult to make. These two facts rule out iron of high purity as a common construction material. Steel, basically an alloy of carbon and iron, on the other hand, is produced in enormous quantities and can be made with a wide range of mechanical properties. Since it is the carbon in steel which is primarily responsible for its mechanical properties, the constitution of steel is perhaps best understood in the light of the iron-carbon equilibrium or constitutional diagram.

The Iron-Carbon Phase-equilibrium Diagram. This diagram is shown in part in Fig. 3-3. In interpreting this diagram, it must be kept in



FIG. 3-2. Photomicrograph showing grain boundaries in solid solution of iron and nickel, 200X. (E. E. Schumacher, Bell Telephone Laboratories, Inc.)

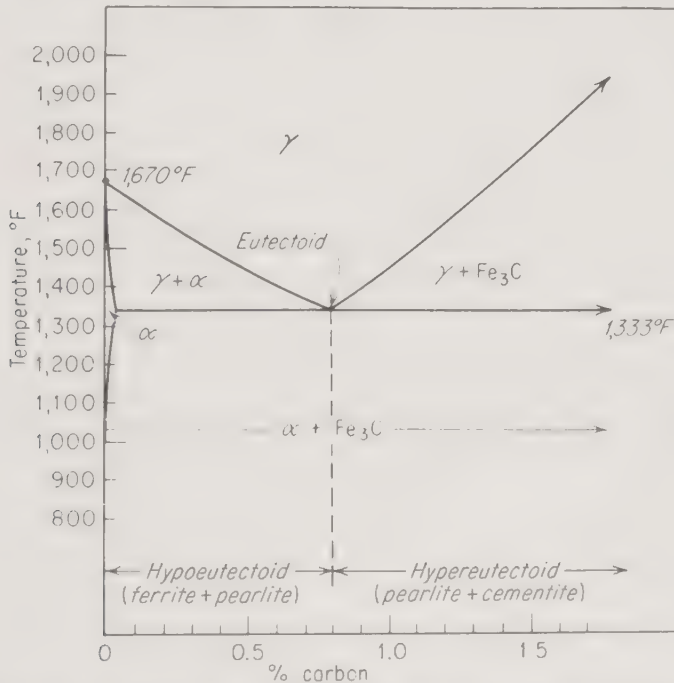


FIG. 3-3. Important part of the iron-carbon phase-equilibrium diagram. γ phase = austenite; α phase = ferrite; Fe_3C = cementite; eutectoid = pearlite.

mind that it shows the phase-equilibrium relationships between the various phases made up of iron and carbon which can exist under the conditions indicated. Only that portion of the diagram is shown which is important in the heat-treatment of steels, and it includes only solid phases. The liquid phase (as well as several others) lies above the diagram shown in Fig. 3-3.

The portion of the diagram labeled γ represents a solid solution of carbon in iron, stable in this region, which is called *austenite* or the γ phase. It is made up of carbon dissolved in γ iron, which has the face-centered cubic lattice structure. It will be observed that there is a minimum temperature (about 1330°F) at which austenite can exist as a stable phase, and it can exist alone at this temperature only when the composition is 0.8 per cent carbon. This is known as the *eutectoid* composition, and it divides steels into two classes—hypoeutectoid and hyper-eutectoid—which behave differently as they are cooled.

When austenite having a carbon content below 0.8 per cent (hypoeutectoid) is cooled slowly, it eventually reaches a temperature where γ iron begins to transform into α iron, which has the body-centered cubic lattice structure. The solid solution of carbon in α iron which is formed is known as *ferrite* or the α phase. It contains very little carbon because carbon is only slightly soluble in α iron. Thus, the remaining austenite has a higher carbon content, which lowers its transformation temperature. This transformation continues as the temperature is lowered further until the eutectoid temperature is reached, at which point the steel consists of a mixture of low-carbon ferrite and of austenite having the eutectoid composition. Further cooling results in the isothermal transformation of the remaining austenite into ferrite, with carbon being rejected from solution as *cementite* (Fe_3C). The ferrite and cementite so formed are intimately mixed into a characteristic structure known as *pearlite*. Thus, the two constituents which are observed microscopically at room temperature in a hypoeutectoid steel which has been slowly cooled are ferrite and pearlite. Figure 3-4 shows a photomicrograph of such a steel in which the light areas are ferrite and the laminated structure is pearlite. The cementite appears dark in these laminations.

When austenite having a carbon content above 0.8 per cent (hyper-eutectoid) is cooled slowly, it eventually reaches the saturation temperature for carbon dissolved in γ iron. Continued cooling results in the rejection of carbon as cementite, and the remaining austenitic phase is lowered in carbon content. This process continues until the eutectoid temperature is reached, at which point the steel consists of a mixture of cementite and austenite of the eutectoid composition. Further cooling causes the austenite to transform isothermally to pearlite as before. A photomicrograph of such a steel is shown in Fig. 3-5. The light material surrounding the pearlite is cementite.

The addition of other elements alters the equilibrium diagram, but the principles remain the same.

Heat-treating Carbon-steel. So far, only the phase-equilibrium cooling of steel has been considered, and, as we have seen, the only products of this process are ferrite, cementite, and a mixture of the two known as



FIG. 3-4. Photomicrograph of hypoeutectoid steel showing ferrite (light areas) and pearlite (laminated areas), 1,000 \times . (From G. M. Enos and W. E. Fontaine, "Elements of Heat Treatment," John Wiley & Sons, Inc., New York, 1953.)

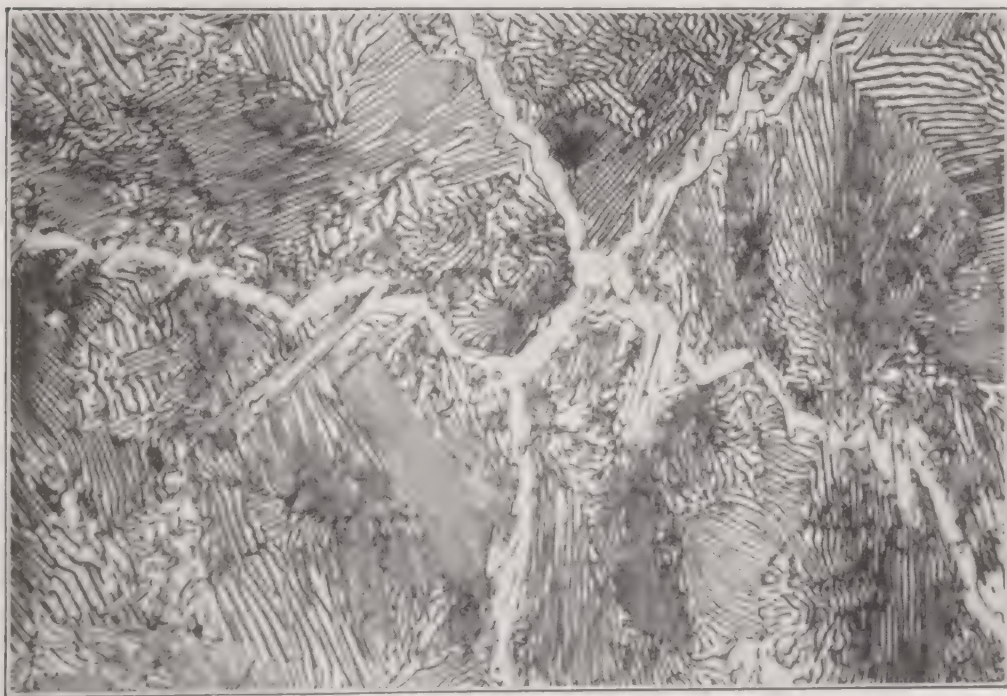


FIG. 3-5. Photomicrograph of hypereutectoid steel showing pearlite and cementite, 1,000 \times . (From "The Making, Shaping and Treating of Steel," 6th ed., United States Steel Company, Pittsburgh, Pa., 1951.)

pearlite. Actually, slow cooling, or *annealing* (which must be done under controlled conditions in a furnace), approaches phase-equilibrium cooling, but this is only one of a number of heat-treatments⁵ to which steel may be subjected. If all steels were annealed, the range of physical properties attainable would be very limited. The other heat-treatments used involve nonequilibrium cooling, and they lead to the formation of several different products having characteristic microstructures and properties. All hardening operations involve the more or less rapid cooling of austenite



FIG. 3-6. Microstructure of tempered martensite, 1,000 \times . (From G. M. Enos and W. E. Fontaine, "Elements of Heat Treatment," John Wiley & Sons, Inc., New York, 1953.)

through the temperature range where phase transformation is indicated by the equilibrium diagram. If cooling is rapid enough, transformation cannot occur at the indicated temperatures but takes place rather at lower temperatures and forms pearlite, bainite (generally considered to be a very fine form of pearlite), or martensite, depending on the conditions of cooling.

The most commonly used heat-treating operations are called *quenching* and *tempering* (drawing). When properly carried out, the cooling rate during the quench is high enough to prevent transformation of the austenite until a low temperature (about 450°F) is reached. At temperatures below this, the austenite transforms to a product called *martensite*,

⁵ G. M. Enos and W. E. Fontaine, "Elements of Heat Treatment," John Wiley & Sons, Inc., New York, 1953.

which is an unstable supersaturated solution of carbon in a distorted α -iron lattice. Under the microscope, this material appears to have a needlelike structure. It is a very hard and brittle material in which high residual stresses exist. It is invariably tempered, i.e., heated to temperatures below the α - γ -transformation temperature and held there for a time. This relieves the residual stresses left by transformation and rapid cooling and causes carbide precipitation from the supersaturated solution. Tempered martensite has the highly desirable properties of high strength and good ductility. Its microstructure is shown in Fig. 3-6.

A comparison of physical properties, shown in Table 3-2, of a plain

TABLE 3-2†

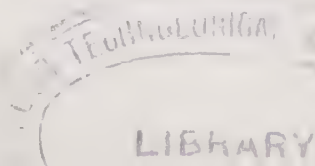
Treatment	Yield strength, psi	Tensile strength, psi	Elongation in 2 in., %	Reduction in area, %	Brinell hardness
Annealed	58,000	94,000	24	53	187
Quenched and tempered . . .	80,000	107,000	24	57	223

† From G. T. Williams, "What Steel Shall I Use?" The American Society for Metals, Cleveland, Ohio, 1941.

carbon steel containing 0.60 per cent carbon as annealed and as heat-treated shows the advantage of the latter. While the ductility is about the same, the yield and tensile strengths, particularly the former, have been significantly increased by heat-treatment. Other combinations of properties, including much higher strength, may be obtained by tempering at different temperatures.

If the quench does not result in sufficiently rapid cooling, transformation of the austenite will occur at higher temperatures, usually to form pearlite which need not have the eutectoid composition but which may be fine or coarse depending on conditions. Pearlite formation is generally to be avoided in quenching since it is not the desired product. Thus, the rate of cooling is of primary importance in determining whether or not martensite will be formed. In carbon steels, this cooling must be very rapid indeed to avoid the formation of pearlite, and in practice it is unattainable unless the piece being quenched is rather small, because the required heat-transfer rates cannot be reached with large pieces. Thus, in quenching a section more than an inch or so in diameter, a considerable decrease in hardness from the surface to the center will be obtained. Carbon steels are therefore said to be shallow-hardening or to have low *hardenability*.

Heat-treating Alloy Steels. This brings us to the subject of alloy steels, for the major purpose of alloying elements, other than carbon, in heat-



treatable steels is to increase hardenability or, to put it another way, to decrease the rate of cooling required for the production of martensite.

Hardenability must not be confused with hardness. The maximum hardness attainable by heat-treatment, assuming the required cooling rate can be attained, is determined mainly by the carbon content. This

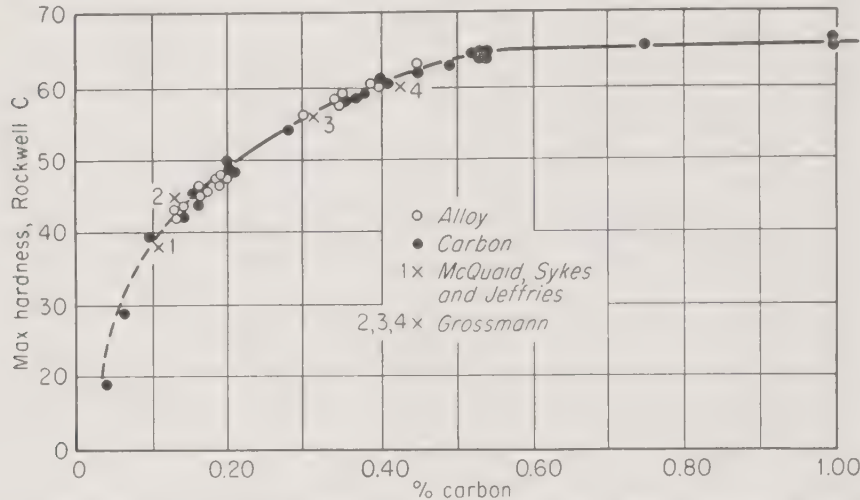


FIG. 3-7. Maximum hardness attainable in carbon and alloy steels as a function of carbon content. (From J. L. Burns, T. L. Moore, and R. S. Archer, *Trans. Am. Soc. Metals*, 26:1 (1938).

maximum hardness is affected by alloy content (up to moderate amounts) to only a very minor degree. The hardenability, or depth of hardening, on the other hand, is almost entirely dependent upon the alloy content. These two different properties are shown in Fig. 3-7 and Table 3-3.

TABLE 3-3†

Steel SAE number	Diameter of bar which will harden to center ($R_c = 50$), in.	
	Water quench	Oil quench
1040	$\frac{3}{4}$	
1340	$1\frac{1}{4}$	$1\frac{1}{16}$
2340	$1\frac{3}{8}$	$\frac{7}{8}$
3140	$1\frac{5}{8}$	1
3240	4	3
X4340	6	4

† From G. T. Williams, "What Steel Shall I Use?" p. 121, The American Society for Metals, Cleveland, Ohio, 1941.

All the steels listed in Table 3-3 have approximately the same carbon content, and all can be heat-treated to give the same hardness and strength provided the required cooling rate can be attained. The size

of bar for which this cooling rate is attainable varies with the type of steel, as shown in the table. Note also that a water quench is more severe than an oil quench. However, some steels cannot be water quenched because of a tendency to crack.

The SAE numbers given in this table represent a classification of carbon and alloy steels adopted by the Society of Automotive Engineers and also by the American Iron and Steel Institute (AISI). These numbers indicate the composition of the steels. The first digit designates the type of steel: 1 means carbon steel, 2 means nickel steel, 3 means nickel-chromium steel, etc. The second digit usually indicates the percentage of the major alloying element, and the last two digits indicate the points, or hundredths of a per cent, of carbon in the steel. Thus SAE 2340 steel is a nickel steel containing 3.5 per cent nickel and 0.40 per cent carbon. A letter preceding the number conveys added information. For example, the X preceding 4340 in Table 3-3 indicates a special chemical composition slightly different from the usual 4340 steel. For a full list of the SAE or AISI steels, the reader should refer to one of the standard handbooks.^{2,3,6a}

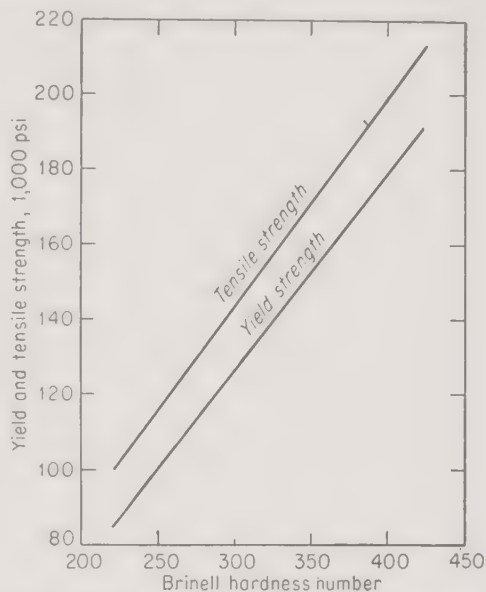


FIG. 3-8. Approximate relation between tensile and yield strengths and hardness for carbon and low-alloy steels in the hardened and tempered condition. (From *"The Making, Shaping and Treating of Steel,"* 6th ed., United States Steel Company, Pittsburgh, Pa., 1951.)

In summary, it is clear that a choice of steel, assuming it is to be hardened, depends in large measure on the size of section being considered. The maximum tensile properties which can be developed, however, depend largely on the carbon content. The tensile properties actually developed will depend on the particular tempering temperature used and will be related to the hardness developed approximately as shown in Fig. 3-8. The advantages of quenched and tempered steels with their high strength and ductility will become apparent from a study of Chap. 6.

Effect of Heat-treatment on Machinability and Internal Stresses. There are two other factors which must be considered in connection with the heat-treatment of steels. They are machinability and internal stresses

^a (a) J. H. Perry, editor, *"Chemical Engineers' Handbook,"* 3d ed., pp. 1543-1547, McGraw-Hill Book Company, Inc., New York, 1950; (b) *ibid.*, pp. 1539-1543.

resulting from heat-treatment, and they are related. Machinability depends on a number of factors such as composition and heat-treatment, and different steels at the same hardness do not necessarily have the same machinability. In general, as hardness increases in quenched and tempered steels, machinability decreases. Thus, the question arises as to whether to heat-treat first and then machine or to machine first and then heat-treat. The difficulty with the former is that machining may be troublesome. The difficulty with the latter is that the internal stresses developed by heat-treatment may cause warpage, and even if this does not occur, there will be a slight change in dimensions. No general answer can be given to this problem. It is sometimes advantageous to do the rough machining before heat-treatment and the finishing after heat-treatment even though this may require grinding.

Internal stresses resulting from heat-treatment are important in the design of pressure vessels. When a piece of steel is quenched, cooling is not uniform throughout the bar, and volume changes therefore do not occur uniformly. There are two volume changes to be considered, the contraction due to cooling and the expansion which occurs when austenite transforms into its low-temperature products. Both changes occur in a nonuniform manner throughout the piece and may set up large internal stresses of various patterns depending on conditions. The patterns developed in cylinders by quenching are discussed by Wishart.⁷

Effect of Other Treatments on Properties of Steel. There are several other factors which should be mentioned in connection with the metallurgy of steel. All solid steel is formed initially as a casting and as such has certain undesirable properties. In the first place, unless the molten metal is deoxidized, or "killed," usually with aluminum, carbon monoxide gas is given off during freezing, and gas bubbles are frozen into the solid metal. Unkilled, or "rimmed," steel is ordinarily severely hot-worked (rolled at elevated temperatures), and this working largely eliminates the gas pockets and fuses the metal surfaces together. Nevertheless, for high-pressure equipment, rimmed steel should probably be avoided. Killed steels give less trouble with gas pockets; however, they suffer from other deficiencies common to all castings. These are "segregation" or nonuniformity, large grain size, and high internal stresses. Furthermore, castings may be difficult to heat-treat, though considerable progress has been made in this respect in recent years. Through careful heat-treatment, the above deficiencies in the original casting may be largely eliminated. Nevertheless, castings are not often used as such in high-pressure equipment.

The alternative to castings is wrought steel, which is made by hot-

⁷ H. B. Wishart, "Residual Stress Measurements," pp. 97-117, American Society of Metals, Cleveland, Ohio, 1952.

or cold-working of the original casting, usually followed by heat-treatment. Through working, uniformity is promoted. Furthermore, controlled hot-working followed by careful heat-treatment gives a controlled grain size in the final product. Grain size is another factor which has a bearing on the properties of steel. In general, small grain size is desirable, for it promotes both strength and toughness.

Another method of strengthening steel aside from heat-treating is cold-working, and this may be accomplished even with plain, low-carbon steels which are not heat-treatable. The main effect of cold-working is an increase in yield strength, which may be more than doubled by moderate cold-working. Tensile strength and hardness are also moderately raised, and ductility decreases somewhat. Cold-working naturally sets up stresses within the metal, but these stresses are not uniformly distributed. Uniformity may be promoted and the properties of the metal may be improved by a so-called stress-relieving anneal—heating to a temperature of 600 to 950°F. This treatment must not be too long or at too high a temperature, or all benefit of cold-working will be lost. Williams gives data to show the results of moderate cold-working and stress-relieving on SAE X1335 steel; these are given in Table 3-4.

TABLE 3-4†

Condition	Tensile strength, psi	Yield strength, psi	Elongation in 2 in., %	Reduction in area, %
Hot-rolled	92,000	57,000	28	59
Cold-worked only	133,000	82,000	11	41
Cold-worked and relieved 600°F	136,000	114,000	14	41
Cold-worked and relieved 950°F	115,000	98,000	19	47

† From G. T. Williams, "What Steel Shall I Use?" The American Society for Metals, Cleveland, Ohio, 1941.

Steels differ in their susceptibility to strengthening by cold-working. In this, chemical composition plays a part, but there seem to be no general rules.

A special application of cold-working for strengthening pressure vessels is the process of autofrettage, discussed in Sec. 6-2. To autofrettage a vessel, a pressure sufficient to make it yield is applied internally. Thus the maximum yielding occurs at the inner surface or bore. When the pressure is removed, a stress pattern remains in the vessel varying from tension in the outer fibers to compression on the inner fibers, an advantageous stress pattern. It might seem strange that special effort is sometimes made to autofrettage a vessel when it is a process that will occur automatically in service whenever the stress exceeds the yield strength.

The explanation is that a stress-relieving anneal similar to the one used after cold-working is used to improve the properties of the vessel further. As a matter of fact, several cycles of applying pressure and heating are frequently used. This is said to "stabilize" the vessel. Its object is to restore elasticity to the metal, which is apparently accomplished by relieving microstresses set up by the plastic flow. Naturally the treatment is designed to leave the major, or macro-, stress pattern largely intact. Actually, no more than a small increase in bursting pressure can be achieved in this way, but the vessel can be made to behave elastically to much higher pressures.

High-alloy and Stainless Steels. The SAE and AISI alloy steels contain no more than moderate amounts of alloying elements—below 5 or 6 per cent. There are many other steels available in this same alloy range made by individual steel companies. In addition, there are a large number of unclassified steels of high-alloy content available such as high-speed tool steels. Information on these steels is best obtained from the steel companies or from standard data books. One of the most useful sources of data for all kinds of steels and other metals and alloys is Hoyt.^{8,9}

The so-called stainless steels deserve special mention. The word "stainless" is a relative term and implies only superior resistance to rusting and corrosion. The specific element largely responsible for this property is chromium, and it is generally present in an amount greater than 12 per cent.

There are three general classes of stainless steels. They are:

1. *Martensitic:* Iron-chromium-carbon alloys which can be heat-treated to give the martensitic structure.
2. *Ferritic:* Iron-chromium-carbon alloys which have the ferritic structure and which cannot be hardened by heat-treatment.
3. *Austenitic:* Iron-chromium-nickel alloys which exist as austenite at low temperatures. Carbon content is invariably low and, for all practical purposes, is an impurity. These steels are nonmagnetic and cannot be hardened by heat-treatment.

These steels are classified by type numbers by the American Iron and Steel Institute. All austenitic types have numbers in the 300 series, i.e., 303, 316, 347, etc. Ferritic and martensitic stainless steels have type numbers in the 400 series.

The austenitic steels are the most common type of stainless steel and are usually what is meant by an offhand reference to stainless steel. The most common type is known as 18-8 and contains about 18 per cent

⁸ S. L. Hoyt, "Metal Data," Reinhold Publishing Corporation, New York, 1952.

⁹ S. L. Hoyt, editor, "ASME Handbook: Metals Properties," McGraw-Hill Book Company, Inc., New York, 1954.

chromium and 8 per cent nickel. As mentioned above, these steels cannot be hardened by heat-treatment, but they are very susceptible to work-hardening and can be greatly strengthened by this process. In addition to their excellent corrosion resistance, these steels have other special properties which recommend them for use under unusual conditions of temperature, both high and low.

3-4. Special Alloys. Other metals besides steel are available, but none is so widely used where high strength is required. When they are used, it is usually because they possess some special property such as corrosion resistance or high-temperature strength. There are a few special alloys which approach the room-temperature strength common in steels. Most of these alloys owe their high strength to a process known as precipitation-hardening, which occurs when particles of an alloying element or an intermetallic compound separate out of a supersaturated solid solution. In their initial manufacture, such alloys are usually cooled rapidly, so that precipitation of these particles does not occur. In this form, the metal is relatively soft and can be machined. It is then heated to a prescribed temperature and held for a time during which precipitation of the aforementioned particles takes place. These apparently act in some way as stress raisers and confer hardness and strength on the metal. This process is also known as "age-hardening." Familiar age- or precipitation-hardening alloys are duraluminum (a few per cent copper in aluminum), beryllium-copper (about 2 per cent beryllium in copper), K Monel (an alloy of nickel, copper, aluminum, and titanium), Inconel X (titanium and aluminum in a nickel-chromium alloy), and stainless W (titanium and aluminum in an austenitic stainless steel).

There are also a number of complex alloys used for their corrosion and heat resistance. Examples are the Hastelloys, Stellites, Chromax, and Nichrome. A number of these are listed by Perry,^{6b} and Hoyt^{8,9} gives extensive data.

3-5. High-temperature Properties of Metals. The properties of metals are temperature-dependent at any temperature, but the effect becomes more marked at elevated temperatures. Thus, when steels or other alloys are to be used at temperatures above 700 or 800°F, the results of the common room-temperature tests cannot form a basis for design. The reason for this is that most metals flow slowly, or *creep*, under stress at such temperatures. Thus, the rate of creep, determined by a "creep test," becomes the decisive factor in design of equipment for high-temperature service, for there must be a practical limit to the amount of flow allowable in a metal under load. The most common way of expressing this limit is to restrict the stress for a given temperature to values below that which will give a creep rate (rate of elongation of a specimen under constant tension) of 1 per cent in 10,000 hr (more than a

year) or of 1 per cent in 100,000 hr, etc., depending on the application. Of course, the metal must not break at these allowable deformations, and this is confirmed by the *stress-rupture* test.

In making this test, constant loads well above those allowable in design are applied to samples in tension until they fail, the time for failure being recorded as a function of load and temperature. The advantage of this test is that it can be carried out in a reasonable time, whereas creep tests at usable loads cannot usually be carried to failure because of the time involved. However, the creep test is basic, and it is the one which should be relied upon in design. An extrapolation of stress-rupture data back to usable stresses is frequently made, though many authorities question the value of results so obtained.¹⁰

Creep rates of steels naturally depend upon composition, with small additions (1 or 2 per cent) of molybdenum or tungsten being particularly beneficial. Steels for high-temperature service must be completely killed, or deoxidized. In contradistinction to room-temperature service, steels for use at elevated temperatures are most satisfactory when the grain size is large, and the preferred heat-treatment is not quenching and tempering but *normalizing*—cooling in air from the austenitic region. This heat-treatment can be controlled to give the desired grain size.

Of the steels, the austenitic stainless types have the best high-temperature properties. Special alloys such as Inconel X, the Hastelloys, Monel, etc., have been developed specifically for use at high temperatures. Detailed data on these materials may be obtained from their manufacturers or from data books.

Most corrosion problems are magnified at high temperatures because reaction rates are increased. Rapid scaling by oxidation in air occurs with carbon and low-alloy steels at high temperatures. This is another reason for the use of stainless steels and special alloys, but even these materials are not immune to trouble under certain conditions. A common difficulty encountered with austenitic steels is carbide precipitation at the grain boundaries. This occurs when these steels are held in the temperature range 950 to 1250°F for even relatively short periods. Since this carbide is rich in chromium, its formation depletes the steel near the grain boundaries in this element and renders these areas susceptible to intergranular corrosion and possible deterioration. This may be prevented by “stabilizing” the carbide by addition of columbium or titanium to the steel or by using a very low carbon content.

There are any number of special corrosion problems which may arise because of the use of high temperatures. There may be carburization or decarburization, oxidation, pitting, thermal fatigue, corrosion fatigue,

¹⁰ H. W. Gillett, “The Behavior of Engineering Metals,” p. 337, John Wiley & Sons, Inc., New York, 1951.

etc. Many of these problems are discussed by Rutherford,¹¹ and he concludes that most service failures are brought on by localized or temporary overheating, i.e., heating to temperatures above those for which the metal was selected. Equipment for high-temperature use cannot usually be designed for indefinite service, but rather is designed for a definite life.

3-6. Effects of Gases on Metals at High Pressure. It has been known since the advent of the Haber process for synthesizing ammonia from its constituent elements that hydrogen-bearing gases at high pressures and temperatures can attack steel. Since that time, much empirical information has been published about the effect of both ammonia-synthesis gas and hydrogen gas on steels and other metals.

There seems to be contemporary agreement on the mechanism of high-temperature hydrogen attack. Several steps are involved. First, hydrogen in the atomic state is adsorbed on the surface of the steel. It then enters the lattice of the metal, evidently becoming ionized in the process. The protons thus formed pass interstitially through the lattice. Over a period of time, they react with the carbon present in steel to form methane, which collects at the grain boundaries and builds up internal pressure until it exceeds the cohesive strength of the grains. The grains are thus forced apart, resulting in a permanent alteration of the mechanical properties of the steel through intercrystalline cracking, fissuring, blistering, and decarburization. These manifestations of hydrogen attack can usually be detected by microscopic examination as well as by mechanical tests.

This discussion will be centered around the effects of hydrogen; but it is not to be inferred that hydrogen is the only gas capable of acting on steel, nor should it be assumed that the deleterious effects of a hydrogen-bearing gas are a direct function of the hydrogen content. Ammonia-synthesis gas in its action on steel is generally considered to be more severe than hydrogen alone, for all the manifestations of hydrogen attack may be present in pronounced degree, and in addition nitriding of the steel often occurs. Hydrogen in the presence of hydrogen sulfide is believed to be a more active corrodent than hydrogen alone; and carbon monoxide is a very severe corrodent at high pressures in the presence of hydrogen even at relatively low temperatures.¹² Various other agents such as sulfur, arsenic, cyanides, and moisture have been mentioned as promoters of hydrogen attack.

Since carbon is involved in the mechanism of attack, there are two obvious methods of trying to prevent hydrogen attack. One is the use

¹¹ J. J. B. Rutherford, "High Temperature Properties of Metals," pp. 133-170, American Society for Metals, Cleveland, Ohio, 1951.

¹² G. A. Nelson, *Trans. ASME*, **73**:205 (1951).

of low-carbon steel, and the other is the addition of alloying elements which combine with carbon to form very stable carbides. The former method alone has not shown much promise, but the latter method has met with considerable success. The strongest carbide-forming elements are titanium, vanadium, zirconium, columbium, tantalum, and thorium. Chromium, molybdenum, and tungsten are quite beneficial.

It is difficult to summarize the available information concerning hydrogen attack because of the number of variables involved. Nelson¹² has presented results graphically as maximum safe temperature vs. hydrogen partial pressure for several common steels. These curves are shown as leveling off at pressures of 3,000 to 4,000 psi, indicating that higher pressures are not correspondingly more severe in promoting hydrogen attack. The temperatures at these leveling-off points are as shown in Table 3-5. The implication is that these steels may be used without

TABLE 3-5

	Temp., °C
Plain, low-carbon steel.....	220
1% Cr, 0.5% Mo, and 0.5% Mo steels.....	330
2% Cr, 0.5% Mo steel.....	400
3% Cr, 0.5% Mo steel.....	540
6% Cr, 0.5% Mo steel.....	610

danger of attack at temperatures below those listed at any pressure. Other tests, however, indicate that this is not the case.¹³ For example, a 5 per cent chromium, 0.5 per cent molybdenum steel showed a marked effect of hydrogen after exposure for several weeks at only 475°C to hydrogen at 2,000 atm.

At pressures of 2,000 atm and above, an effect known as hydrogen embrittlement becomes evident even at room temperature. This effect is distinct from hydrogen attack in that it apparently does not involve a chemical reaction, but is rather a physical embrittlement caused by the hydrogen itself. It causes no change in microstructure of the metal, but may alter its mechanical properties drastically and cause unexpected failure in a brittle fashion.

Austenitic stainless steels seem to be practically immune to both hydrogen attack and hydrogen embrittlement. However, they are nitrified by nitrogen gas at high pressure and temperature.¹⁴

Figures 3-9 to 3-11 show examples obtained by the author¹³ of the effects of hydrogen on metals. Figure 3-9 is a photograph of two tensile specimens, rejoined after breaking, which were made of Nichrome Alloy V and which were originally the same. Each specimen had a hole drilled

¹³ H. C. Van Ness and B. F. Dodge, *Chem. Eng. Progr.*, **51**:266 (1955).

¹⁴ H. K. Ihrig, *Ind. Eng. Chem.*, **41**:2516 (1949).

TABLE 3-6

Treatment	Tensile strength	Reduction in area, %	Elongation in 2 in, %
Heated sample.....	96,100	54	53
Sample exposed to hydrogen.....	52,000	15	6

along its axis from one end so as to form a small pressure vessel. The sample on the right was subjected to an internal hydrogen pressure of 2,000 atm for 4 weeks at 475°C, while the sample on the left was only heated during this time. The effect of hydrogen on the ductility of this material is evident and is also shown in Table 3-6 by a comparison of properties from the tensile test. This result is typical of tests run on

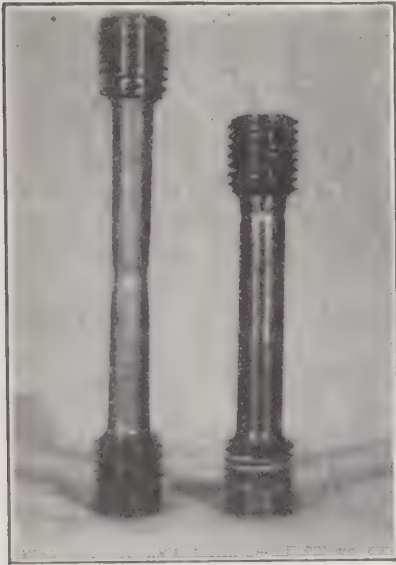


FIG. 3-9. Tensile specimens of Nichrome Alloy V. Original length, 4 in.; diameter of reduced section, $\frac{1}{2}$ in. Sample on the right exposed to hydrogen at 2,000 atm and 475°C for 4 weeks. Sample on left was heated only.



FIG. 3-10. Photomicrograph of a low-alloy steel exposed to hydrogen for 1 week at 1,000 atm and 425°C. Unetched, 25 \times .

several nickel-base alloys containing little iron—Nichrome Alloy V, K Monel, Inconel, Inconel X, and Hastelloy B. None of these materials was satisfactory under severe conditions. Chromax and Nichrome, on the other hand, contain less nickel and more iron and were not attacked at the conditions used.

Figure 3-10 is a photomicrograph of the inner edge of a polished but

unetched tensile specimen of a low-alloy steel subjected to a hydrogen pressure of 1,000 atm at 425°C for 1 week in the manner described above. The dark lines are cracks which, in general, follow grain boundaries. This steel contained 0.50 per cent carbon, 0.65 per cent chromium, and 0.18 per cent molybdenum. It was very severely attacked.

Figure 3-11 is a photomicrograph of a section cut from a check valve which failed at room temperature under a hydrogen pressure of 3,000 atm. It was made of hardened AISI 4140 steel. There seems to be no explanation for this failure other than hydrogen embrittlement. There were several fine radial cracks in this valve, only one of which is shown in

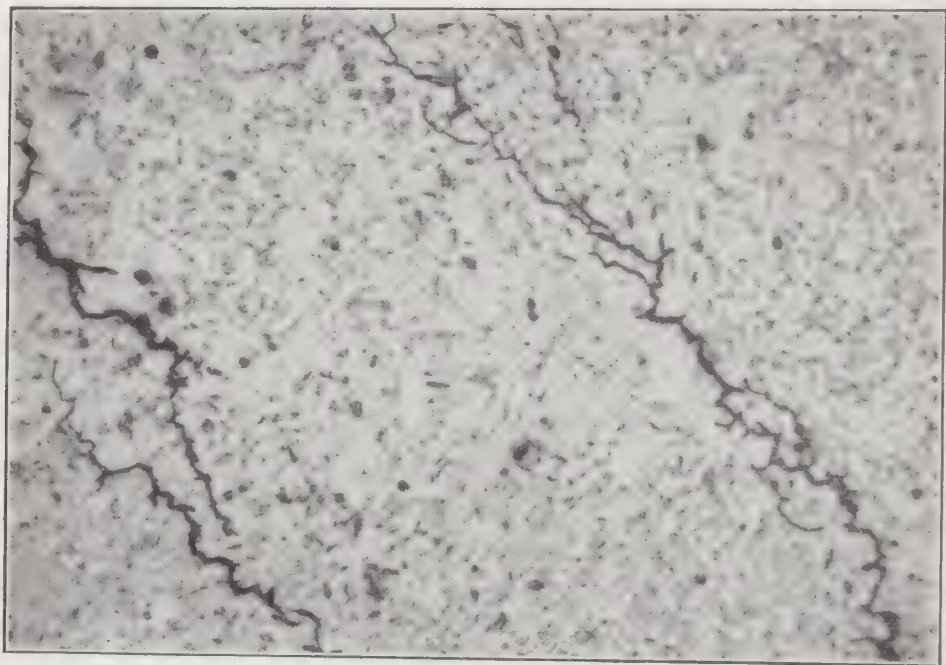


FIG. 3-11. Photomicrograph of cracked check valve. AISI 4140 steel, hardened to R_c of 35, etched with picral, 250 \times .

Fig. 3-11. Subsequent tests showed that many materials can be dangerously embrittled at room temperature by hydrogen at pressures as low as 2,000 atm. Experiments run at pressures up to 4,000 atm showed austenitic stainless steels to be unaffected. Furthermore, parts of the equipment made of beryllium-copper and austenitic steels gave no trouble.

There is much yet to be learned about the effects of gases on metals. However, it is certain that caution is well advised where high-pressure hydrogen is to be used either at room temperature or at high temperature. For either case the use of austenitic stainless steels is recommended.

CHAPTER 4

SAFETY

Proper consideration of the hazards involved during the design, layout, and operation of equipment for use at high pressures can make such equipment as safe as equipment for use at low pressures. The possible hazards are due to flying fragments from the failure of high-pressure vessels, fittings, and gauges and to the toxic effects or secondary gas explosion resulting from the release of gases when such failure occurs. Reasonable precautions consist of making certain that the equipment is adequately designed, maintained, and operated for the purpose for which it is used and located so that the effects of a failure will be localized and of minor consequence.

4-1. Barricades. A failure, especially when occurring under high gas pressure, can be expected to project metal parts or fragments with high velocity. Barricades may be used to avoid injury to personnel and damage to other facilities. If the failure releases explosive gases, the ignition of these may result in more extensive damage than that caused by the flying fragments. If an explosion occurs, the explosion pressure can be released through a lightly constructed wall.

An arrangement providing both barricades and a light explosion wall is illustrated by the high-pressure laboratory shown in Figs. 4-1 and 4-2. The operators' gallery runs through the center of the building, with offices and service rooms on one side and cells for high-pressure equipment on the other side. These cells are surrounded on three sides by 1-ft-thick reinforced-concrete walls and are closed on the outer side by a lath-and-tar-paper blowout wall. The blowout walls, in this case, face a hill which provides ample protection for the other buildings. One cell with 3-ft-thick concrete inside walls is provided for especially hazardous experiments. Entrance to these cells is through sliding doors of $\frac{1}{2}$ -in. boiler plate. This type of construction is suitable for fairly large-scale pilot-plant operations where the quantity of material handled is large enough to create appreciable hazard if a failure of the equipment occurs. It is good practice to avoid enclosing a high-pressure cell completely on all sides, top, and bottom with heavy walls. Rather, one

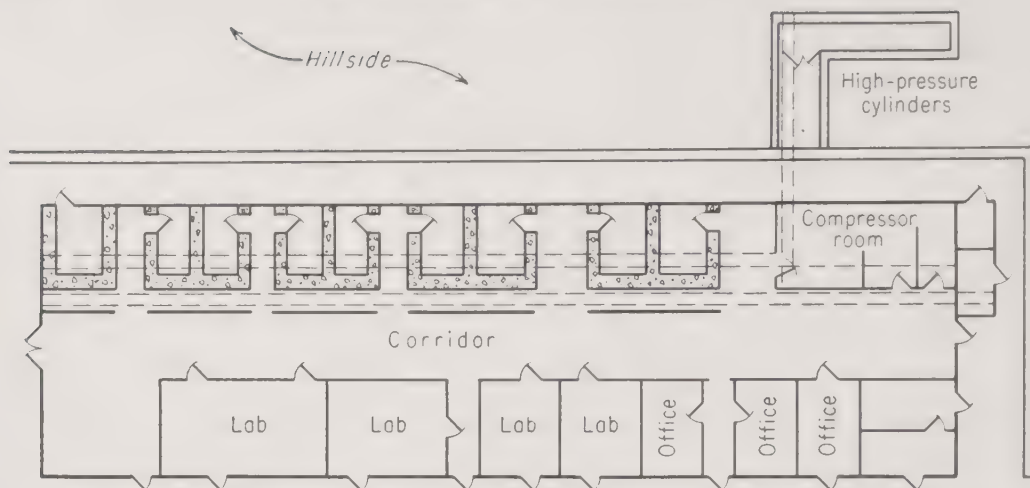


FIG. 4-1. Floor plan of a high-pressure laboratory. (*Hercules Powder Company.*)

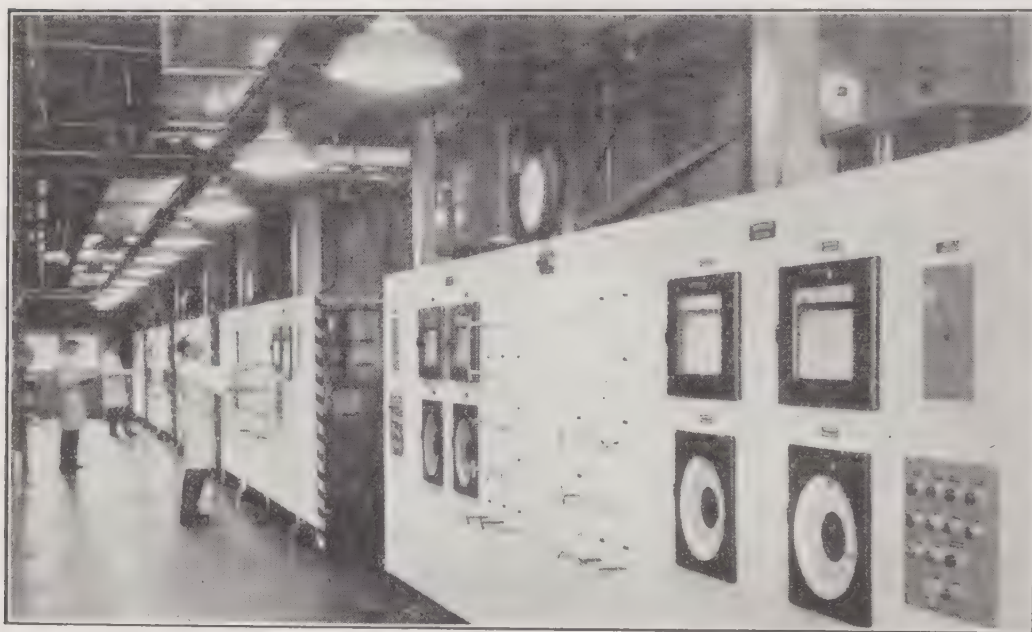


FIG. 4-2. View of the operators' gallery in a high-pressure laboratory. [*From Chem. Eng. News*, 27(11):777 (1949); *Hercules Powder Company.*]

direction should be provided in which a large expansion of gas may be vented.

The design of a barricade to give protection against flying fragments or missiles can be based on the design of protective structures developed by the United States Navy.² There are three main factors to be considered:

1. The velocity of the missile at impact
2. The physical properties of the missile
3. The characteristics of the material of the barricade

² "Design of Protective Structures," Navy Docks P-51, Department of the Navy, Bureau of Yards and Docks, Washington, August, 1950.

One of the relations which takes these factors into account is the modified Petry equation

$$D = kA_p \log \left(1 + \frac{V^2}{215,000} \right) \quad (4-1)$$

where D = depth of penetration, ft

k = experimentally determined coefficient of penetration, cu ft/lb

A_p = sectional pressure, weight of the missile divided by its maximum cross-sectional area, psi

V = impact velocity, ft/sec

A few values of k are as follows: concrete (mass concrete with a crushing strength of 2,200 psi), $k = 7.99 \times 10^{-3}$; reinforced concrete (normal reinforced concrete with a crushing strength of 3,200 psi and 1.4 per cent reinforcement), $k = 4.76 \times 10^{-3}$; especially reinforced concrete (with a crushing strength of 5,700 psi and 1.4 per cent reinforcement),

$$k = 2.82 \times 10^{-3}$$

stone masonry, $k = 11.72 \times 10^{-3}$; brickwork, $k = 20.48 \times 10^{-3}$; sandy soil, $k = 36.7 \times 10^{-3}$.

The depth of penetration given by Eq. (4-1) represents a minimum penetration as obtained with a barricade mass with a thickness three or more times the penetration. The equation is not valid when the missile perforates the mass. The minimum thickness to avoid perforation is twice that given by Eq. (4-1), or $2D$. Steel plates used in combination with concrete may be considered as having a protective value such that a 1-in.-thick ordinary-structural-grade steel plate is equal to a 12-in. thickness of concrete of about 3,000 psi strength. For especially treated steel, the equivalence is about 1 in. to 18 in. of concrete.

For small-size experimental units and when unknown chemical reactions in large volume are not involved, a steel barricade may be employed with the experimental apparatus mounted behind it as shown in Fig. 4-3. Instruments not subjected to high pressure, such as ammeters, voltmeters, recording pyrometers, and switches, and also gauges for the lower-pressure parts of the system are mounted on the face of the panel. Access to essential parts such as valves may be provided by small doors in the panels. A few of the frequently used control valves may be provided with extensions to the valve stem which pass through the panel preferably at a level above the operator's head. When the processes do not involve a chemical reaction and are on a small scale at moderate temperatures and pressures, ample safety factors may be provided in the design of the apparatus and the barricades may be dispensed with.

The thickness of the steel barricade required is indicated by the ballistic-penetration data given above. A considerable saving in the weight of steel may be made by reinforcing local areas subject to the

greatest hazards with thick wood planking, or by using layers of sand held between light wood or metal walls. In some cases, thick steel barricades have been bolted to a rigid angle-iron framework. An explosion behind the barricade then exerts a great pressure on it and may shear the bolts, scattering the heads about the laboratory like projectiles. It is safer to weld the steel sheets to the framework or, when bolts are used, the heads should be welded to the plates.

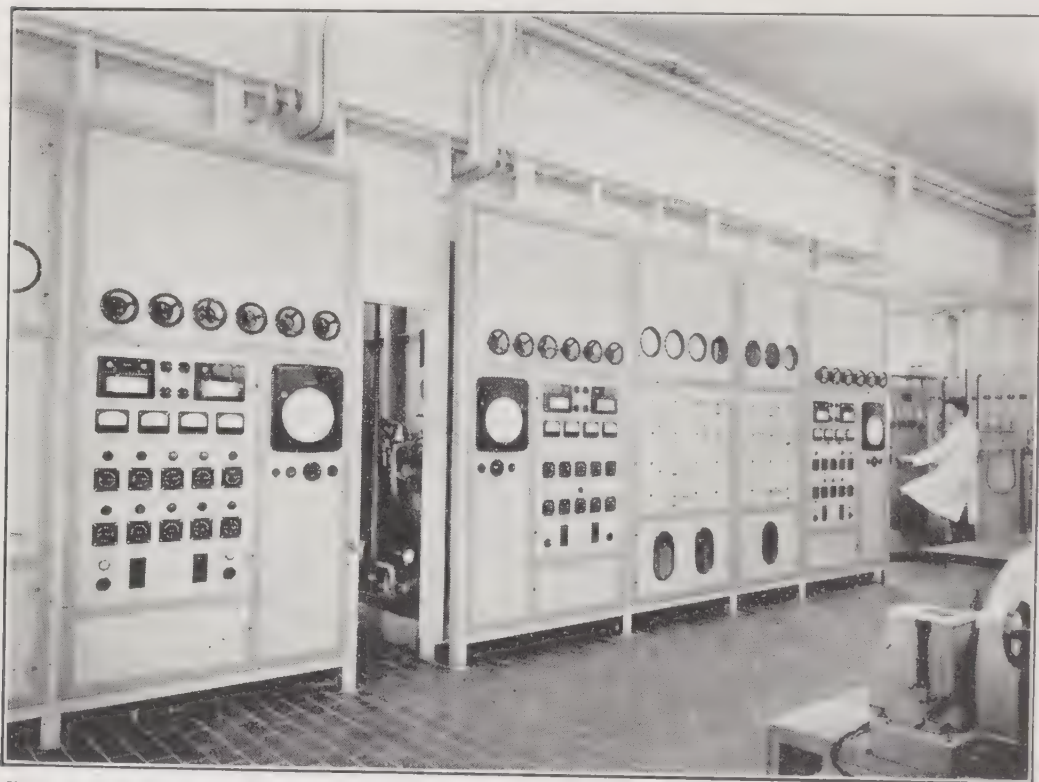


FIG. 4-3. Panel board for 60,000-psi autoclaves. A 1-in. steel barricade separates the autoclaves and valves from the panel board. (From A. Guyer, *Swiss Federal Institute of Technology*.)

4-2. Equipment Hazards. Experience has shown that several items of equipment are the major source of accidents when dealing with high pressures. High-pressure valves have at times caused accidents and deserve consideration both as to their location and operation. The valve stems have been projected from the valve body with considerable violence and can cause injury or even death to personnel in the line of fire. The valves should be considered part of the high-pressure equipment and installed behind the barricades with the stems pointing upward or away from the operators. A shaft through the barricade may be used to operate a valve through a worm-gear drive as shown in Fig. 4-4. If the valve stems are brought through the barricade, they should be at a level above the operator's head. Key valves in the system, subject to fre-

quent use, should be remotely controlled through a mechanical, electric, or hydraulic linkage. When high-pressure tubing fails, it has been known to whip about the room, causing damage and creating a serious hazard. This may be prevented by securely anchoring all tubing.

Bourdon pressure gauges supplied by reliable manufacturers can normally be depended upon to be in excellent condition when received. Conditions outside the control of the supplier have at times led to their failure. The practice of manifolding several gauges handling pressures in both low and high ranges makes it easy to open the wrong valve and subject a low-pressure gauge to high pressures. Corrosion, fatigue of the metal, and shock waves due to explosions in the equipment have all

led to gauge failure. In some installations, the gauges are installed behind the barricade and are read through a system of mirrors, which protects the operator from flying glass or metal fragments. Some gauges are provided with a light metal door hinged at the back. This is intended to provide for venting gases through the back of the gauge in case of a failure. Care should be taken in mounting such gauges to allow freedom for this door to open. Such a gauge cannot be mounted flush on a panel board. The glass face of the gauges may be removed and replaced with transparent plastic to avoid the danger of flying glass. In operation, gauges may be filled with the gas under investigation or they may contain oil or other liquids. Filling the gauge with oil tends to minimize corrosion and to reduce the hazards in case of failure, since the effect of expanding gases is avoided. The sudden application of high gas pressure to a gauge may cause a substantial increase in temperature due to the adiabatic compression of the gas. When the gauge is subject to rapid changes in pressure or to fluctuating pressures, a throttling device should be provided to avoid fatigue of the metal. A check valve or surge valve will prevent too rapid a rise or fall of pressure. The transducer,³ strain gauge,⁴ and other devices⁵ make it possible to install the pressure element behind the barricade and record its movements on an instrument operated electrically or pneumatically on the face of the panel.

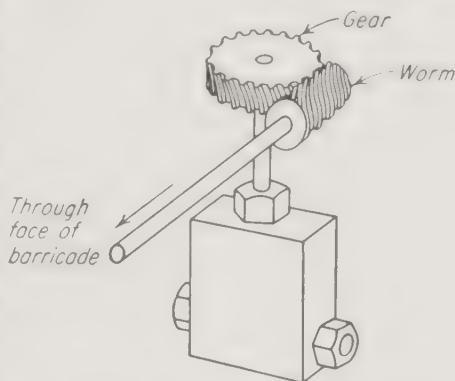


FIG. 4-4. A gear-driven valve stem as a safety feature.

³ *Statham Laboratories, Inc., Bull. P10, Los Angeles, Calif. (1955).*

⁴ *Baldwin-Lima-Hamilton Corporation Bull. 306 and 4107, Philadelphia, Pa.*

⁵ "Microsen Pressure Transmitter," Catalog 400A, Manning, Maxwell and Moore, Inc., Bridgeport, Conn.

Pressure Relief. All high-pressure reaction and process vessels should be adequately equipped for the release of unexpectedly high pressures. In small experimental systems for the measurement of physical properties, this release may be provided in the tubing connections away from the main vessel. But in larger-size vessels, the openings for relieving liquid and especially gas pressures should be as close to the largest volume of these fluids as is possible. This usually requires that the pressure-release device be installed in the main walls or head of the vessel itself. Two types of pressure release in common use are the spring-loaded safety valve and the rupture disk. The rupture disk provides a weak spot in the wall or head of the vessel carefully designed to fail at a pressure somewhat lower than the limiting pressure for the vessel itself. This type has found favor because of its positive action, large venting capacity, and the rather small likelihood that it can be prevented from functioning at the proper time. These disks are usually dished to provide for uniform stress distribution. They may even be hemispherical in shape. When the disk ruptures, there is no means of shutting off the vessel until the pressure has fallen to that of the atmosphere. When the vessel contains only a gas under high pressure, this results in the complete loss of the contents of the vessel. The disk as a whole or fragments of it may possibly be ejected with considerable force, and consideration should be given during installation to avoid injury or damage from these slugs. The disk may be designed to rip open or tear, in order to avoid projecting slugs of metal. A design of rupture disk is shown in Fig. 5-24. Corrosion may weaken the disk to some extent and cause it to rupture at a pressure below that for which it is designed. A proper inspection and replacement schedule will provide for this contingency. Dodge⁶ has pointed out that the working pressure in the vessel produces stresses close to the yield point of the material in the disk. This tends to cause strain-hardening with the result that the disk may fail to relieve at the pressure for which it is designed.

A spring-loaded safety valve frequently gives trouble because it is not entirely self-seating. It is a rather large and bulky unit when built in sizes adequate to handle emergency volumes of gas. In the smaller sizes, designs have been perfected which are satisfactory from the self-seating standpoint. Valves of this type are especially useful in relieving pressures which increase rather slowly and provide adequate warning that normal conditions are being exceeded.

In order to avoid the loss of the contents of a large vessel and at the same time provide complete pressure-release protection, two pressure-release devices may be used in parallel. One of these is set to release

⁶ B. F. Dodge, in J. H. Perry, editor, "Chemical Engineers' Handbook," 3d ed., sec. 18, McGraw-Hill Book Company, Inc., New York, 1950.

at a lower pressure than the other; the lower-pressure-release device is then provided with a shutoff valve, and the device itself is usually of somewhat smaller venting capacity than the higher-pressure release. The lower-pressure release may be either a safety valve or a small-capacity rupture disk, provided with a shutoff valve between it and the main vessel. Such a valve should never be installed if this is the only pressure-release protection, since there is always a possibility that it may be shut off inadvertently at the moment the release is required. If the pressure increase is not stopped by the lower-pressure device, the higher-pressure, large-capacity release will then function and empty the contents of the vessel.

It is as important to provide lines of adequate capacity to carry off the vented gases or liquids to a safe place as it is to provide for the release of pressure. Poorly designed pressure-release devices have functioned and protected a high-pressure vessel, only to have the vented gases escape into the room and cause a secondary explosion destroying a major portion of the plant.

Miscellaneous. In laying out any plant, provisions must be made for emergency shutdown due to failure in one unit. Some pieces of equipment cannot be shut down instantly without damaging them. Provisions should therefore be made to continue these in operation for a period of time long enough to take them out of operation without damage. This applies especially to equipment which has a high heat capacity relative to that of the material being processed through it. Direct-fired tubular stills or vessels together with their firebrick setting are examples of this class. Provision must be made to continue circulating fluid until the heat of the setting and vessel or tubes is absorbed and the temperature reduced below that at which coking and charring of the contents will take place.

High-pressure gas compressors and circulating pumps of commercial size are usually housed in a compressor room, without special barricades. Small compressors for research may be protected by barricades. Adequate ventilation should be provided in the compressor area. Leakage or rupture of lines and fittings is most likely to occur in this area due to the vibrations from the compressors. The compressor is normally connected to large storage or reaction vessels, and these may be vented to the compressor area through such a leak even though the compressor is not operating. In the hypercompressor stages, there is a tendency to pinch off the piston rods. Where the pistons are aligned by carrying the rod through a gland in the head end, there is danger of this rod being sheared and projected from the cylinder.

In experimental work, there is a tendency to make one piece of equipment serve a number of purposes. There is no objection to this practice;

however, it should be pointed out that there are no safe short cuts to the careful review of all features of the unit to determine whether it is properly designed for each application. Hastily conceived, makeshift applications are extremely hazardous in operations at high pressure. A complete description of the unit and its history is valuable when reviewing the design for a new application.

When calculating the capacity of a vessel to be filled with liquid, the thermal expansion of the liquid should be a matter of careful concern. It is very easy to subject the vessel to excessive pressures if too little void space is allowed when filling it at low temperatures. Raising the temperature then causes the liquid to expand and overstress or rupture the vessel.

The tensile strength of most metals increases at low temperatures, but they frequently become brittle and subject to fracture and the development of cracks. Equipment subjected to temperatures below 0°F and especially the low temperatures of solid carbon dioxide and liquid air should receive careful consideration from this aspect. Welds should be especially well annealed. Only metals and alloys found to possess good low-temperature properties should be used. When chilling combustible liquids or gases to low temperatures by using liquid air, there is a hazard arising from a possible leakage of these materials into the liquid air. Proper barricading may be provided, or liquid nitrogen may be substituted for liquid air as a cooling medium.

4-3. Hazardous Compounds and Mixtures. Reactor failures in the laboratory can usually be attributed to exothermic reactions such as polymerizations, oxidations, and the like. Often the best means of carrying out highly exothermic reactions is a tubular reactor of small cross section and relatively great length operated continuously at rather high flow rates.

Certain compounds have shown a tendency toward spontaneous reaction when subjected to high pressures. These reactions are usually accompanied by the evolution of heat and the generation of explosive pressures. A partial list of such compounds would include butadiene, ethylene oxide, dioxane, and acetylene. It is the compression of oxygen especially, and to some extent air, that should be considered as a special problem. Hersey⁷ has discussed the oil-oxygen explosion hazard. The compression of oxygen in the presence of oil cannot be done with safety, and, since most gas compressors are lubricated with oil, oxygen should not be compressed in them. Water may be substituted as a lubricant when the design permits. Experience has shown that an explosion may result from admitting oxygen rapidly at high pressure to a space containing traces of oily matter. When admitting oxygen

⁷ J. Hersey, *Am. Soc. Naval Engrs.*, **36**:231 (1924).

to a space which may contain hydrocarbon matter, the pressure should be built up slowly. When a gas containing finely divided liquid or solid particles is passed over a metal object at high velocity, the object becomes electrically charged. The charge may cause a spark and, if the gas is combustible, an explosion. The rupture of a metal container may be accompanied by frictional effects which cause high local temperatures and ignite combustible gas. A table of the explosive limits of various substances in air will be found in Appendix F.

Carbon monoxide under pressure acts on pure nickel and more slowly on iron, forming the carbonyls. This action may tend to weaken walls made of these materials. Since the carbonyls are gases, the metals may be carried through the system and deposited at some other point on decomposition of the compound. Mercury amalgamates with many other metals and alloys, especially with brass, copper, and zinc. These materials will lose their strength completely when brought in contact with mercury. It is usually thought that mercury has no effect on iron or steel. However, Bridgman⁸ has pointed out that mercury will wet iron surfaces, when these are newly formed by opening cracks in the iron under the mercury surface. Such cracks may develop in a mercury container subjected to pressure and cause severe weakening of the walls. Mercury will penetrate steel and eventually will cause rupture at pressures of about 5,000 atm and above. Under pressure mercury forms a compound with ammonia consisting of several molecules of ammonia per atom of mercury. This compound apparently is not explosive; however, as the pressure is lowered the ratio of ammonia to mercury decreases and a compound similar to a fulminate is formed. This has been known to detonate and is a serious hazard. The hazard is greatest when a system containing mercury and ammonia is being depressurized or the ammonia removed.

4-4. Construction and Maintenance. The design of each piece of high-pressure apparatus should take full account of the effect of the pressures to which it will be subjected and also of other effects such as those of hydrogen, carbon monoxide, and wet carbon dioxide. Each piece of equipment should be and normally is subjected to thorough inspection and testing by the fabricator. However, the limitations imposed by its use are likely to be better known to the investigator, and the responsibility for safe usage should be that of the investigator rather than of the fabricator. Vessels should be carefully examined for small hairline cracks inside and outside and tested for leaks or weak spots by a suitable hydraulic-test procedure using an oil with a high flash point

⁸ P. W. Bridgman, "The Physics of High Pressure," The Macmillan Company, New York, 1931; new impression with supplement, George Bell & Sons, Ltd., London, 1949.

but with especially good penetrating properties. Such an oil is more effective in locating leaks than is water. These tests should be carried to pressures at least 50 per cent in excess of the maximum working pressure and in some cases to several times the working pressure. A method for hammer-testing a vessel while under pressure and filled with the hydraulic-test penetrating oil consists of striking the outside of the wall with hammer blows which are regulated so that their energy in foot-pounds is at least equal to the weight in pounds per square foot of the metal being tested. Such treatment serves to reveal incipient cracks. The technique of using helium and a mass spectrograph to locate small leaks in the vessel walls can be applied to pressure vessels.

An inspection program for new equipment has been outlined by Glasebrook.⁹ A hydrostatic-pressure test should be made on new reactors at 1.5 times the designed maximum working pressure. The diameter of the vessel should be carefully measured with a micrometer three times: first, before the pressure is applied; second, at the test pressure to determine the expansion of the vessel, preferably after the pressure has been applied for an hour; and third, about an hour after the pressure has been released to show any permanent deformation. A stabilizing heat-treatment after the test is recommended by some authorities. The three micrometer measurements should be permanently recorded for future reference. This type of test should also be applied to pumps, receiving vessels, and the like.

The hydrostatic-pressure tests should be repeated periodically, and the micrometer measurements compared with those previously recorded. This comparison will provide an early indication of changes in the vessel. Before each hydrostatic test, a careful inspection should be made for corrosion, erosion, thread wear, hairline cracks, scratches on the closure, scoring of agitator shafts, and any other imperfections. Hydrostatic testing of small vessels is generally considered relatively safe, but the failure of a large vessel under test conditions is hazardous. Vessels should therefore be securely anchored while under test, and the amount of hydraulic fluid under pressure should be reduced by using metal cores or fillers in the vessel being tested.

These periodic tests may be supplemented by strain measurement made during operation. Strain gauges are placed at a number of points on the surface of the vessel when it is installed. The readings from these gauges after subsequent periods of use will serve to indicate the amount of permanent deformation which has taken place and provide a warning before dangerous deformations occur. Sample sections of high-pressure pipeline should be taken from time to time and carefully examined for

⁹ A. L. Glasebrook, "Safety in Study of Chemical Reactions at High Pressures." Catalog 200, Autoclave Engineers Inc., Erie, Pa., 1952.

the growth of internal cracks. Weakening of the walls due to hydrogen attack or to the effect of carbon monoxide may not be readily apparent on inspection. Unusual increases in the external diameter or increased tendencies to leak through the walls of the vessel should reveal such effects before they become hazardous. The ASME and API-ASME codes^{10,11} provide a basis for test and inspection procedures. The ASA¹² issues a code useful for pipe and bombs with an inside diameter of 6 in. or less.

When leaks are noticed in joints or around glands, they should be repaired without undue delay. Leaking glands or closures should never be tightened while under pressure. Such leaks may result in erosion which causes the amount of leak to increase rapidly and to seriously damage the part. On the other hand, they may be due to a cracked or split gasket or badly worn packing rings. In such cases, tightening the joint may cause a serious blowout. Dodge⁶ mentions the hazards which may arise from leaks which contain certain types of catalysts. Some highly active nickel- and iron-catalyst powders are very reactive and oxidize quickly when they come in contact with air. If these leak out through valves or stuffing boxes and become dry, they then glow and may ignite flammable vapors or gases which accompany them. Where continuous leaks of such material are noticed, they should be washed constantly with a stream of water.

4-5. Ventilation. When concentrations of toxic or combustible gases or dusts are present at any point, sooner or later they will ignite or otherwise cause serious injury. Gas pockets or dead-air spaces should be avoided, and adequate ventilation should be provided using forced ventilation if necessary. The laboratory atmosphere as well as gases undergoing processing may be continuously monitored by automatic gas-analysis equipment. The use of explosionproof motors and explosionproof electric lights will minimize the danger of ignition to some extent, but reliance should not be placed entirely on these. There are many cases on record where other sources of ignition such as static electricity, hot spots, and sparks struck by the contact of two metals have caused ignition. The construction of plants out-of-doors when possible is advisable from the ventilation standpoint. When an ignition or explosion hazard is present, it is advisable to use nonsparking tools, clothing and shoes which minimize static-electricity effects, and similar equipment.

¹⁰ "Boiler and Pressure Vessel Code," sec. VIII, American Society of Mechanical Engineers.

¹¹ "Unfired Pressure Vessels for Petroleum Liquids and Gases," American Petroleum Institute and American Society of Mechanical Engineers.

¹² "American Standard Code for Pressure Piping," B 31.1, American Standards Association.

4-6. Personnel Training. Many serious accidents occur from careless or thoughtless action. Instances involve actions such as opening the wrong valve, removing the head from a pressure vessel or pump without first reducing the pressure, and introducing a volatile liquid with combustible vapors into a large vessel which still contains air or oxidizing gases. While the individual operator is, of course, to be criticized for such carelessness, these "accidents" frequently reflect the lack of adequate personnel training and discussion of operating hazards by the supervisory personnel. Every individual who is to operate high-pressure equipment should either make himself familiar with or be instructed in the complete details of the apparatus and connecting lines and the possible consequences of any action he might take. If such training is given initially and refreshed periodically, there should be no more danger in operating high-pressure equipment than in operating equipment used at normal pressures. The responsibility for providing adequate training and an understanding of hazards involved in operating procedures rests on the management. A bibliography on safety practices is available.¹³

¹³ General Safety Committee of the Manufacturing Chemists' Association, Inc., "Guide for Safety in the Chemical Laboratory," D. Van Nostrand Company, Inc., New York, 1954.

CHAPTER 5

EQUIPMENT

A number of examples of apparatus for handling gases and liquids under high pressures will be considered. Such apparatus should provide for measuring pressure, temperature, and other conditions, for sealing pressure vessels by a closure designed to ensure against leakage and, at the same time, to provide for easy access to the inside of the vessel.

[Pressure vessels are connected by pipes or tubing to other equipment, and valves and fittings are installed in the pipes or on the vessels. Compressors are used to elevate the pressure of gases. Apparatus for use at high pressures should be subjected to a suitable testing and inspection procedure before and during its use.]

5-1. Measurement of High Pressures. Pressures in excess of that of the atmosphere are usually expressed in units of atmospheres, millimeters or centimeters of mercury, pounds per square inch, or kilograms per square centimeter. The unit atmosphere is referred to a column of mercury. The international unit is defined as the pressure exerted by a column of mercury, at 0°C , 76 cm in length in a gravitational field giving an acceleration of 980.665 cm/sec^2 . The density of mercury at 0°C is 13.5951 g/cu cm . It is not practicable to determine pressures of the order of several hundred atmospheres by comparing them with a single column of mercury, since a column of the order of $\frac{1}{2}$ mile in height would be required to measure a pressure of 1,000 international atmospheres. Amagat, in his initial measurements of the compressibility of nitrogen, did use such a column of mercury some 900 ft long installed in the shaft of a mine. This resulted in a pressure of the order of 350 atm.

The Dead-weight Gauge. The principal primary pressure gauge is the dead-weight or free-piston gauge. This was originally introduced by Louis Cailletet in 1880 and was modified later by Amagat. The dead-weight gauge has been developed to its present state of precision by a number of others. Four general types of instrument have been described: the simple piston, the reentrant cylinder, the differential piston, and the controlled-clearance piston. The simple piston is shown in Fig. 5-1a and will be used to illustrate the principle of operation. A well-fitting

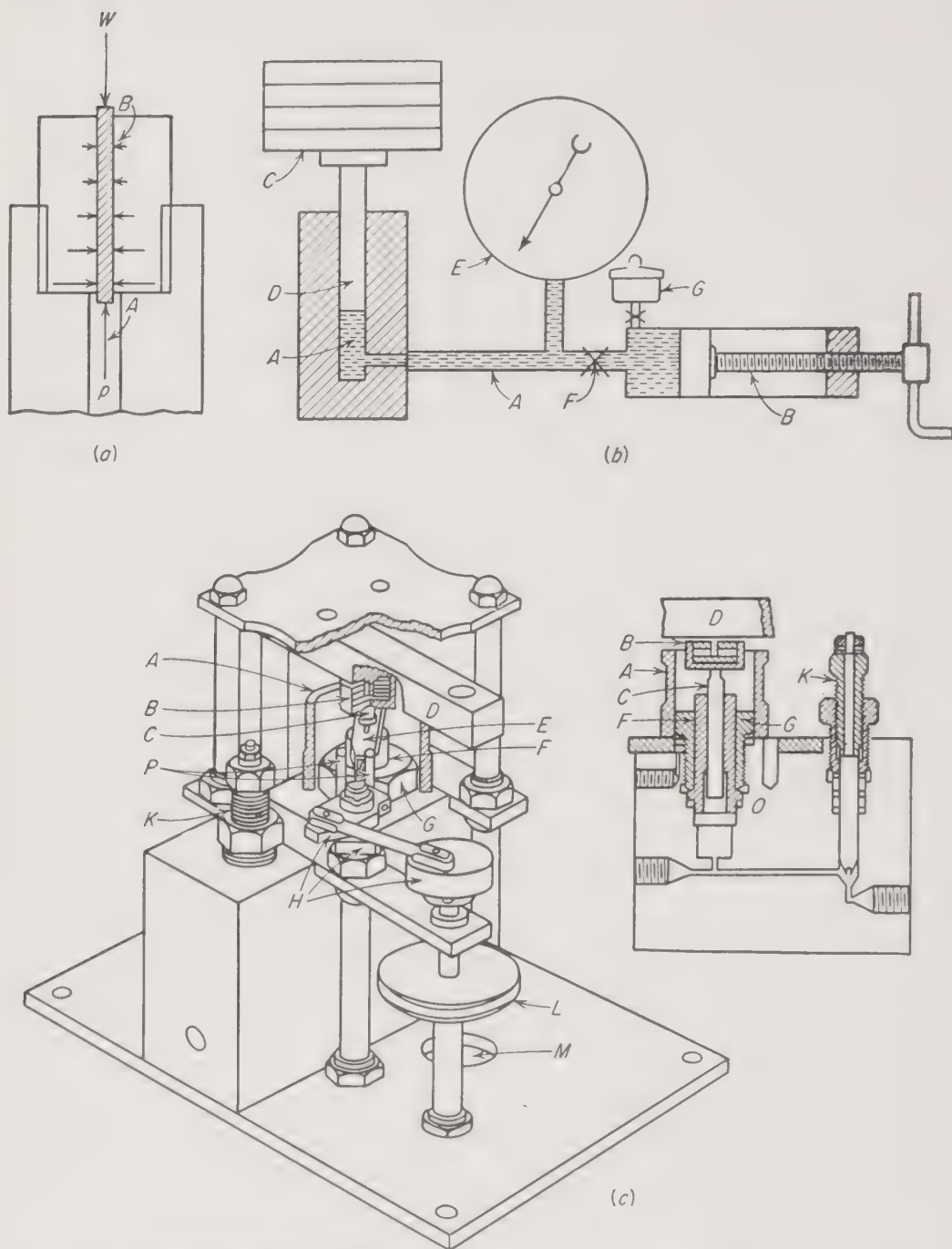


FIG. 5-1. Dead-weight gauge—simple piston type. (a) Principle of operation. (From D. M. Newitt, "Design of High Pressure Plant and the Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.) (b) Assembly with oil injector. (From D. M. Newitt, "Design of High Pressure Plant and the Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.) (c) Interchangeable piston and cylinder. [From F. G. Keyes, *Ind. Eng. Chem.*, **23**:1375 (1931).]

piston slides in the cylinder *B* and serves to close off the lower part of the cylinder, at *A*, which is used as a chamber for oil. Pressure is placed on the oil by applying a known weight *W* to the top of the piston. From a knowledge of this weight and the cross-sectional area of the piston, the pressure *p* on the oil can be readily determined. In Fig. 5-1b, a dead-weight gauge is shown connected for calibrating a Bourdon-type gauge *E*. The sensitivity of the gauge is increased by reducing the friction between the piston *D* and cylinder by rotating the weight *C* and by providing a very small clearance through which a small amount of oil *A* is allowed to

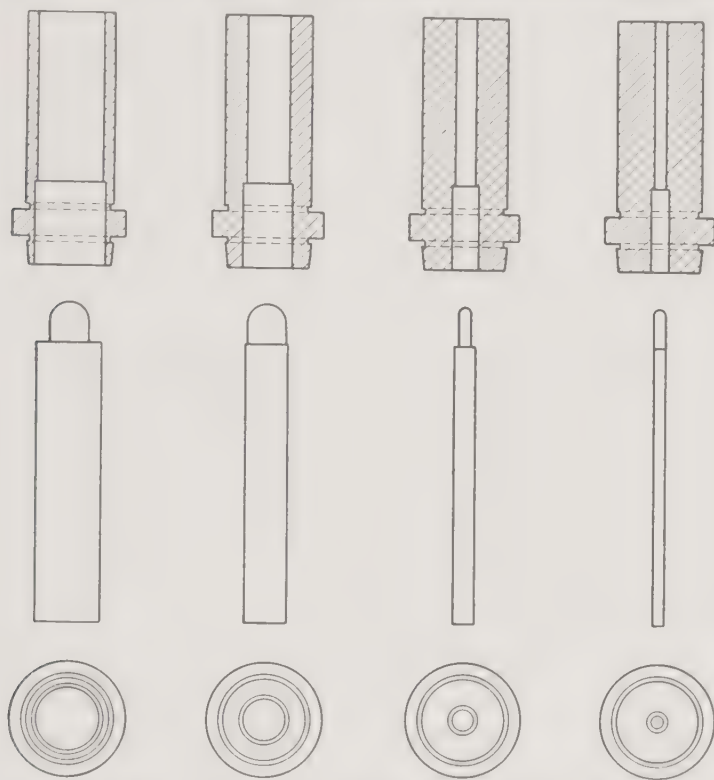


FIG. 5-2. Interchangeable cylinder and piston combinations for dead-weight gauge. [From F. G. Keyes, *Ind. Eng. Chem.*, **23**:1375 (1931).]

leak. Oil is replaced from an injection cylinder *B*, which also generates the high pressure. A cylinder and a piston are shown in more detail in the cross section in Fig. 5-1c. Continuous oscillation of the piston *C* is caused by an arm *E* attached to the top of the piston. This is activated by the system *III*. In this design, the cylinder *F* fits into the gauge block *O* and is removable. A set of replaceable cylinders, each having the same outside diameter, provides for different pressure ranges and makes it possible to maintain a high degree of precision over a wide range of pressure. A set of five pistons and cylinders is shown in Fig. 5-2. This design of gauge is satisfactory for pressures up to 1,500 atm. Both the cylinder and piston are constructed of hardened steel and are ground

and lapped. The diameter is measured with an accuracy of 0.00002 in. In the specifications by Keyes,¹ the piston must not vary more than 10^{-4} cm in diameter throughout its length and must fit the cylinder so that when lubricated it will slide 1 cm/sec under a load of 100 g.

In operation, the gauge is brought to balance in order to measure the pressure of the oil on the piston. When in balance, the piston is stationary because of the equality of the forces acting on it. These forces consist of the pressure of the oil acting on the lower surface of the piston plus the drag of the oil on the walls of the piston as the oil leaks out past the piston. This latter force is equal to one-half the force of the oil pressure acting upward on the small cross-sectional area of the annular space between the piston and the cylinder.² The other half of this force acts on the cylinder wall. These two upward forces are counterbalanced by the force of gravity on the weight on the top of the piston and on the weight of the piston itself as well as the pressure of the external atmosphere acting against the top surface of the piston. This balance of forces is expressed by

$$p \left(A + \frac{a}{2} \right) = (W + w) \frac{g}{g_c} + p_a \left(A + \frac{a}{2} \right) \quad (5-1)$$

where the symbols are as defined in Nomenclature at the end of this chapter.

Rearranging,

$$p - p_a = \frac{(W + w)g}{(A + a/2)g_c} = C(W + w) \quad (5-2)$$

When neither the piston nor the cylinder is distorted by the action of the pressure acting on it, the gauge constant C is independent of the pressure. Calculations based on the elasticity of the steel show that at 1,000 atm distortion of the piston and cylinder involves an error of 1 part in 5,000. To attain this accuracy, the weights used must be carefully calibrated and the temperature of the gauge measured. A 1°C change in temperature causes an error of about 1 part in 55,000. As long as the annular cross-sectional area between piston and cylinder is constant, as it is at pressures somewhat below 1,000 atm, the gauge constant C may be determined by checking the gauge at a single known pressure. O. C. Bridgeman³ has established such a check pressure point for the vapor pressure of carbon dioxide at 0°C , which was found to be 34.4009 ± 0.0013 international atmospheres.⁴ This pressure point was established by

¹ F. G. Keyes, *Ind. Eng. Chem.*, **23**:1375 (1931).

² C. H. Meyers and R. H. Jessup, *J. Research NBS*, **6**:1061 (1931).

³ O. C. Bridgeman, *J. ACS*, **49**:1174 (1927).

⁴ J. R. Roebuck and W. Cram, *Rev. Sci. Instr.*, **8**:215 (1937), obtained a value about 0.05 per cent different from that of Bridgeman.

comparing a number of dead-weight gauges with a column of mercury. The mercury column used was oil-jacketed and had a height of 9 m. In order to attain its full accuracy when the gauge is used at higher pressures, where distortion becomes increasingly important, the constant C must be evaluated by comparison with the pressure difference across a mercury column over the range of pressures and temperatures for which the gauge is to be used. Such a method of calibration has been developed by Holborn and Schultze⁵ and used with two free-piston gauges with pistons of approximately the same diameter.

Other fixed pressure points for use in calibrating these gauges at higher pressures are discussed by Johnson and Newhall.⁶ Bridgman's value¹² of the freezing pressure of mercury at 0°C is 7,640 kg/sq cm with a temperature coefficient of melting of 3,000 psi/°C. He determined the bismuth I-II-phase transition at about 360,000 psi. The four triple points between liquid water and various ices are promising calibration points. These are L-I-III at about 30,000 psi, L-III-V near 50,000 psi, L-V-VI near 90,000 psi, and L-VI-VII near 320,000 psi.

The hardened steel of the piston and cylinder in one instance was observed to undergo an aging process with time.² Over a 10-year period the gauge constant increased by 0.09 per cent, and over a subsequent 10-year period, this increase amounted to 0.02 per cent. There are other instances where no change was observed in 20 years.

A simple type of oil injector is described by Keyes, and a modification of this used by C. O. Bennett at Purdue University is shown in Fig. 5-3. Pressure is developed by turning a large screw by hand which forces a packed steel piston into a lapped hole in a heavy-walled steel cylinder. The cylinder has an outside diameter of about 5 cm. At one end of the cylinder the lapped hole is open to receive the piston; at the other end the hole terminates in a fitting for attaching an oil line. A plug is also provided for filling the injector with oil. The lapped hole is about 1.25 cm in diameter and 30 cm long. It is a few centimeters shorter than the piston. The piston is packed by either of two alternative schemes to prevent oil leakage. In one arrangement the piston carries the packing. A hex-head bolt threaded into the high-pressure end of the piston holds a packing consisting successively of a steel washer, a leather cup washer, and a brass ring. In the second arrangement the packing is stationary. A neoprene O ring backed up by two brass rings is mounted in a groove near the open end of the lapped hole. Both types of packing are suitable for pressures up to at least 2,000 atm.

In either case the piston is attached to the screw through a swivel arrangement which permits the piston to move longitudinally without

⁵ L. Holborn and H. Schultze, *Ann. Physik*, ser. 4, **47**:1095 (1915).

⁶ D. P. Johnson and D. H. Newhall, *Trans. ASME*, **75**:301 (1953).

rotation. This sliding action is more suitable for maintaining a tight seal at the packing than if there were relative turning motion of the packing and the cylinder or piston. The screw coaxial with the piston is about 3 cm in diameter and 45 cm long. It passes through a suitable stationary nut and is provided with spokes for turning by hand at the free end opposite the attachment to the high-pressure piston. Units such as the Blackhawk Porto-Power^{6a} hand pump are available for pressures up to 40,000 psi.

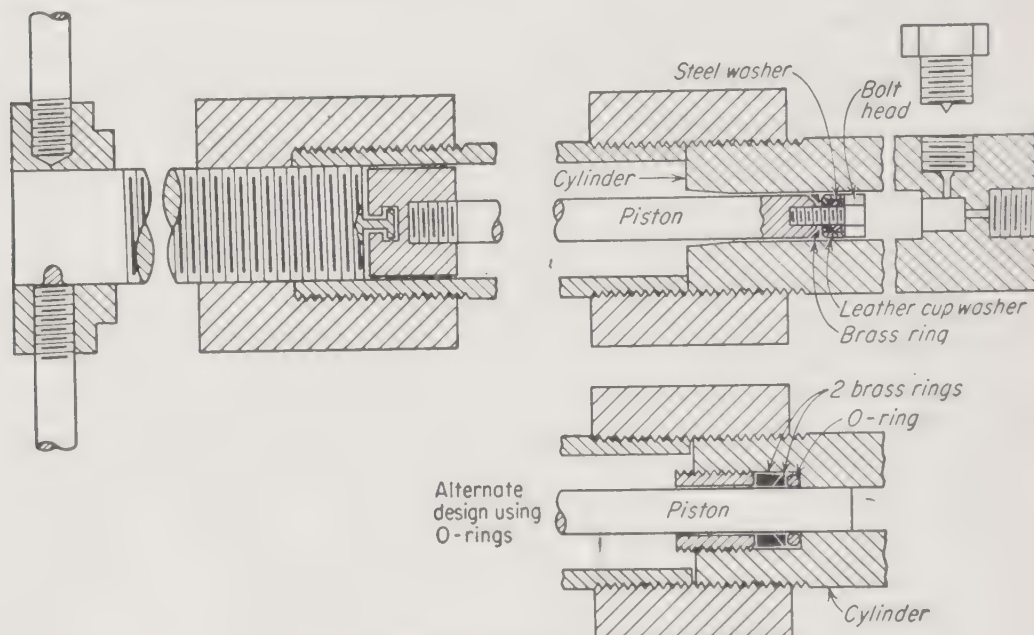


FIG. 5-3. Oil injector.

When the gauge is used to measure the pressure on the piston, it is important to determine rapidly and with certainty when equilibrium between the weights on the piston and the pressure being measured has been attained. Keyes¹ describes a method of accomplishing this. It utilizes a U tube of 3 mm inside diameter placed in a line connecting the gauge to the source of pressure. Mercury in the U tube separates the oil in the gauge from that in the pressure line. An insulated needle at the top of each arm of the U tube serves to indicate the movement of the mercury in either direction by contact between the mercury and the two needles. When too little weight is applied the mercury moves up in one arm and makes contact with one needle, while too much weight causes it to move in the other direction and make contact with the other needle. The current used in these contacts must be very small or there will be a tendency for an emulsion to form between the mercury and the oil. A thyatron may be used to amplify this small current and throw

^{6a} Blackhawk Manufacturing Company Catalog H-201, Milwaukee, Wis., 1955.

a relay in a circuit carrying sufficient current to light a small bulb. With this arrangement, a difference of $\frac{1}{10}$ g can be detected at several hundred atmospheres pressure.

The gauge constant C varies with temperature in such a fashion that the ratio of the constant at temperature t_2 to the constant at temperature t_1 is given by

$$\frac{C_{t_2}}{C_{t_1}} = 1 + 2.2 \times 10^{-5}(t_1 - t_2) \quad (5-3)$$

where t is in degrees centigrade.

The cylinder and piston tend to be distorted by the forces acting upon them. These forces on the piston consist of an axial thrust produced by the pressure inside the gauge and by the weight on top of the piston acting in opposite directions. This thrust is uniform throughout the length of the piston. The piston is also subjected to a variable compressive stress acting radially along its length. This stress varies from the inner end of the piston to the outer and is due to the hydrostatic pressure of the oil in the annular clearance between the piston and the cylinder. There is also a variable hydrostatic pressure acting on the walls of the cylinder distributed in the same manner as that acting on the piston. The hydrostatic pressures tend to expand the cylinder and to compress the piston. The internal radius of the cylinder increases by an amount δ_A due to this internal pressure p_1 as given by

$$\delta_A = \frac{p_1 r_2}{E} \left(\frac{1 + K^2}{1 - K^2} + \nu \right) \quad (5-4)$$

The radius of the piston likewise decreases according to

$$\delta_B = \frac{pk}{3} \quad (5-5)$$

A dead-weight gauge has been designed by Bridgman⁷ which overcomes the distortion of the cylinder to a large extent. This is the reentrant-cylinder gauge. The deformation of the piston does not exceed 0.23 per cent at pressures as high as 13,000 atm. It is estimated that this gauge is accurate to 0.1 per cent at this high pressure. A section through the piston and cylinder is shown in Fig. 5-4a. The piston itself is only $\frac{1}{16}$ in. in diameter to reduce the amount of weight needed. The piston operates in a cylinder of hardened nickel steel which is exposed to the hydrostatic pressure of the oil on the outside of the cylinder as well as on the inside. The cylinder is sealed externally around its upper part by a soft-steel cone rather than on the lower surface as in the gauges for lower pressure. The bore of the reentrant cylinder grows smaller as the pressure is increased regardless of the wall thickness.

⁷ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**:321 (1912).

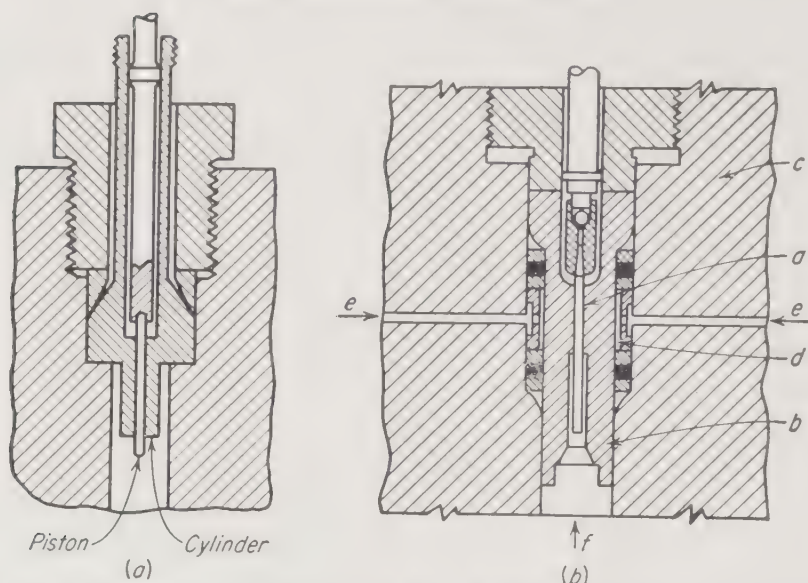


FIG. 5-4. (a) Bridgman's modification of dead-weight gauge for pressures to 13,000 atm. (From P. W. Bridgman, "The Physics of High Pressure," George Bell & Sons, Ltd., London, 1949.) (b) Controlled clearance piston. [From D. P. Johnson and D. H. Newhall, *Trans. ASME*, **75**:301 (1953).]

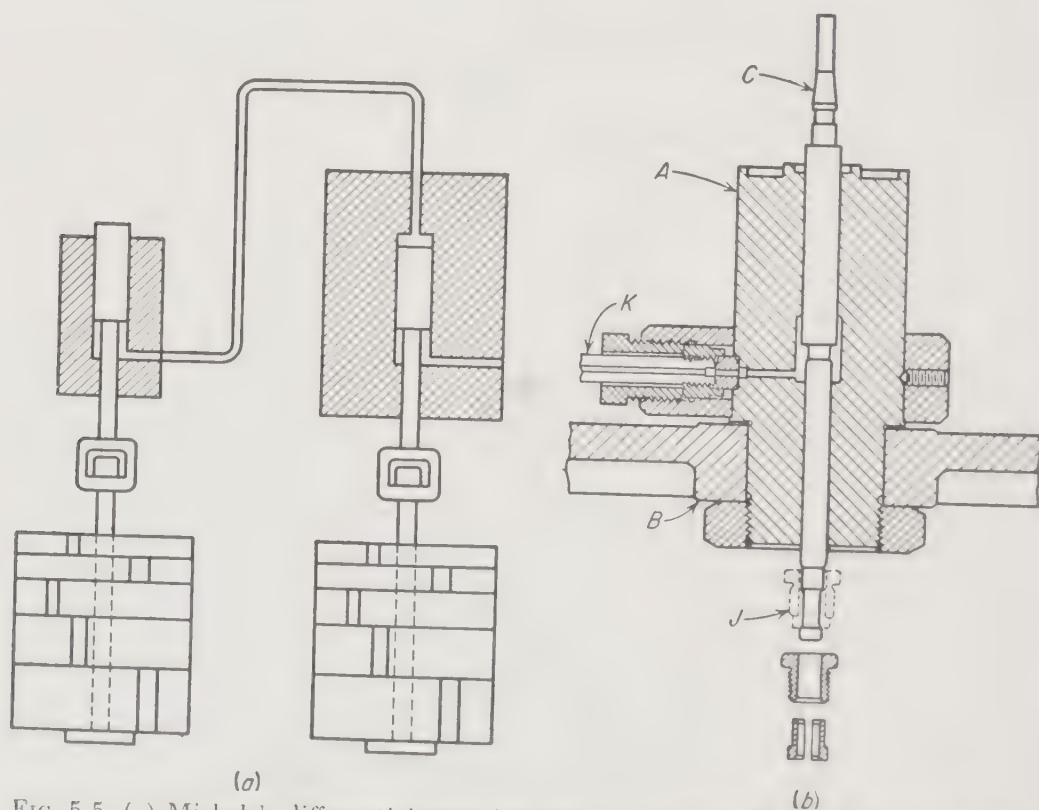


FIG. 5-5. (a) Michels's differential-type dead-weight gauge. [From A. Michels, *Engineering*, **135**:17 (1933).] (b) Pressure balance. (From A. Michels.) (c) Differential-area piston and cylinder. (From A. Michels.)

In a design by Johnson and Newhall the clearance between the piston and cylinder is controlled. This design is shown in Fig. 5-4b. The piston *a* is fitted in the cylinder *b*. The cylinder *b* is enclosed in a chamber in the main block *c* so that a pressure may be applied in the annulus at *d*.

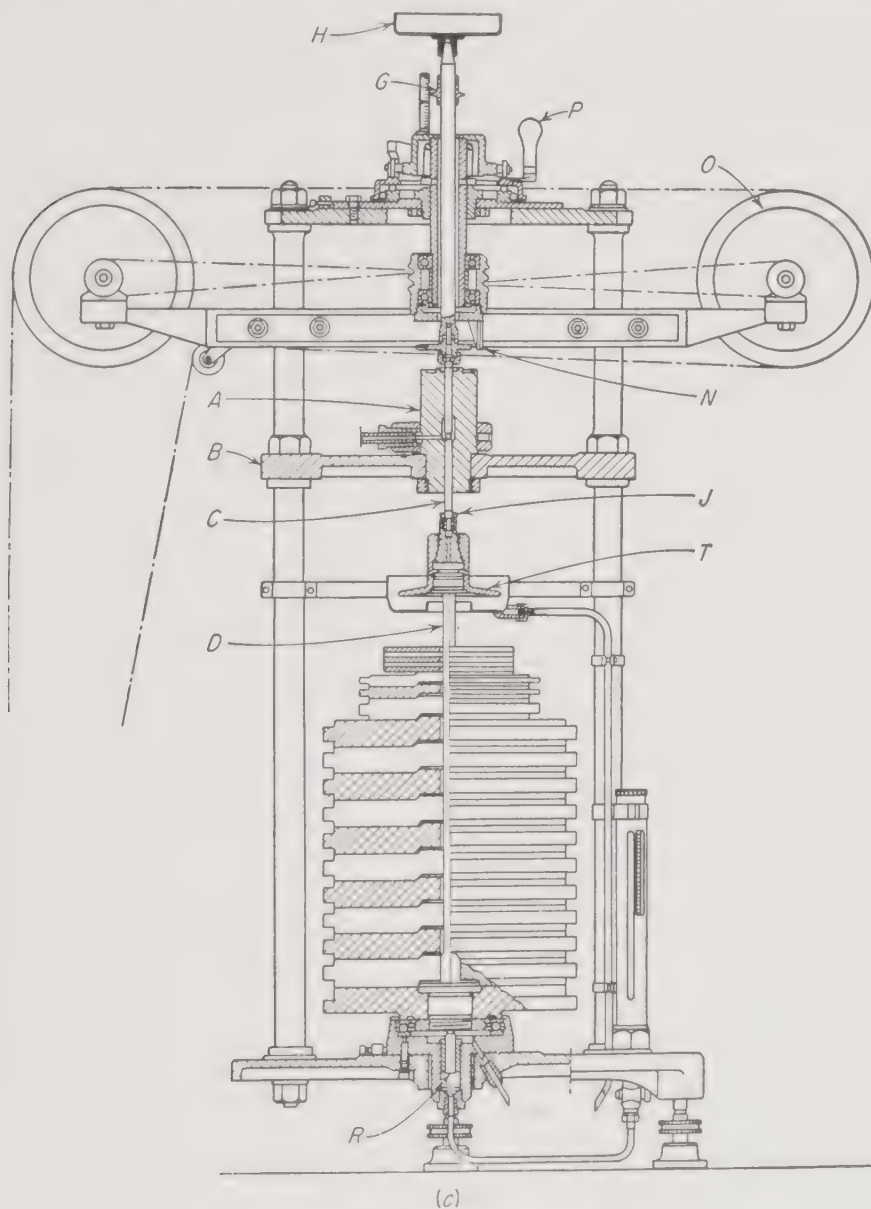


FIG. 5.5. (Continued)

A separate controlled source of pressure is applied at *e*. This pressure is a fraction of that applied to the piston at *f*. The pressure applied at *e* to the wall of the cylinder surrounding the piston may be varied in order to control the clearance between the piston and the cylinder. Leakages as small as 1 cu mm/min at 100,000 psi have been obtained.

The differential-piston gauge was used by Michels.⁸ A series of two sensitive differential-area-piston pressure balances is shown in Fig. 5-5a. The first pressure balance is suitable for pressures up to 3,000 kg/sq cm. The output from this is piped to the upper side of the second piston, and the force developed is added to the dead-weight load. The combined unit is then suitable for pressures up to 10,000 kg/sq cm. The first pressure balance may be used alone with one of its several piston-cylinder combinations. The differential piston is shown in Fig. 5-5b. The cylinder *A* contains two coaxial bores which are fitted with the differential piston *C*. A load is hung on this piston at *J*. The oil pressure to be measured is connected at *K*. The cylinder is supported in the pressure-balance frame *B*. The assembled pressure balance is shown in Fig. 5-5c. The axle *D* carries the main weights. The end of *D* is guided in the bearing *R*. The top end of *D* is connected to the oil shield *T* which also serves to connect the piston and the axle. The piston is rotated in the cylinder to reduce friction. This rotation is provided through the clutch system *N* by leather belts driven by a separate motor and running over the wheels *O*. The clutch is disengaged by turning the handle *P*, and the piston and all weights then revolve freely from their own inertia while a reading is made. The rise and fall of the piston are indicated at *G*. Small weights are placed in the pan *H* to obtain the final balance.

Leakage is controlled by using a close fit between the piston and cylinder. When not under pressure, the piston is tight in the cylinder and does not revolve. When under pressure, the dead-weight load opposes the internal pressure so that the piston is in tension. The tension causes a small decrease in the diameter of the piston and the pressure causes an increase in the diameter of the cylinder. Under these conditions the piston rotates easily.

Bourdon-tube Gauge. The Bourdon-tube gauge is widely used to measure pressure. It is a secondary instrument and must be calibrated against a primary gauge such as the dead-weight gauge. Bourdon gauges are available commercially for pressures up to 80,000 psi. These gauges, when carefully made and calibrated, have an accuracy as good as $\frac{1}{10}$ per cent of the full-scale reading at all pressures except the highest.^{8a} They are available with dial sizes from 2 to 24 in. The basic pressure-indicating element in the gauge is the Bourdon tube. This is a steel tube flattened to an elliptical cross section and bent in the arc of a circle. One end of the tube is closed, and the other end is connected to the source of pressure. The tube, as the pressure is increased, tends to straighten out

⁸ A. Michels, *Ann. Physik*, **72**:285 (1923); *ibid.*, **73**:577 (1924); see also *Engineering*, **135**:17 (1933).

^{8a} Heise Bourdon Tube Company, Inc., Newtown, Conn.

partially, and the movement of the closed end is magnified by a gear-and-pinion arrangement connected to the pointer of the dial.

For the gauges used at the higher pressure ranges, the tube is constructed from a bar of steel and carefully bored on the inside and turned

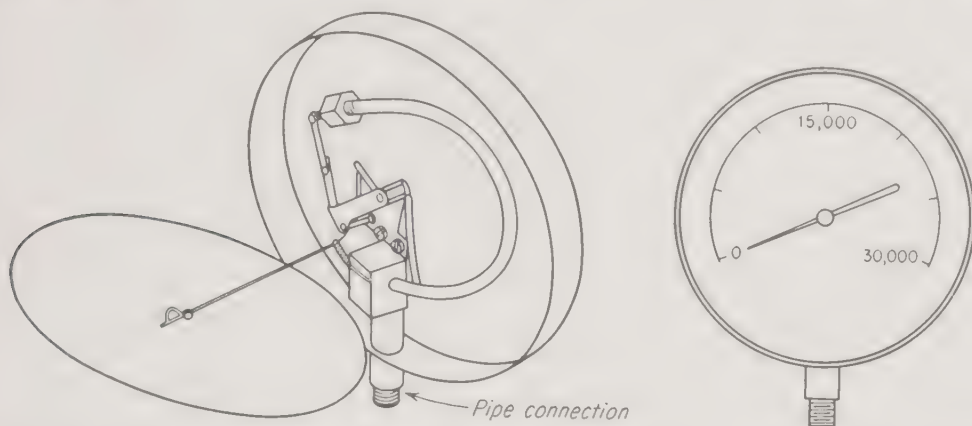


FIG. 5-6. Bourdon-tube pressure gauge with safety back. (American Instrument Company, Inc.)

on the outside to give a uniform wall thickness. It is then flattened in the part between the ends and annealed and hardened. A table of dimensions of Bourdon tubes for various pressure ranges is given in Appendix E. A picture of the back of such a gauge is shown in Fig. 5-6. The Bourdon tube can be seen, as well as the mechanical linkage connecting it to the pointer.

In the higher pressure ranges, the Bourdon gauge tends to give a higher pressure reading when subjected to a given pressure if this is approached from higher pressures than when approached from lower. This hysteresis effect is shown in Fig. 5-7. The effect begins to be quite noticeable at pressures above 2,000 atm and is the cause for the upper limits of the pressure range for which the gauges may be used. For the highest precision, such gauges must be calibrated frequently and for both rising and falling pressures. It is good practice to avoid using Bourdon gauges at pressures higher than one-half to three-quarters of their maximum range.

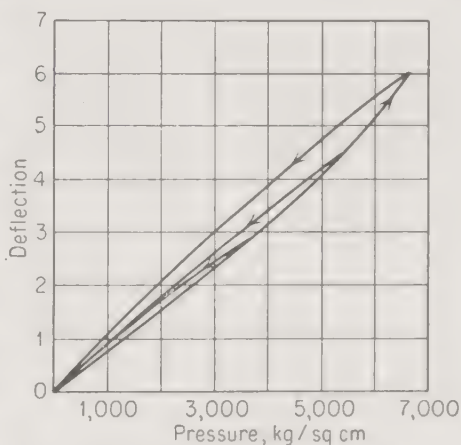


FIG. 5-7. Hysteresis effect with Bourdon-tube gauge. [From P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **44**: 201 (1909).]

Although Bourdon tubes are manufactured with the greatest of care, there is the possibility that a tube may be accidentally overloaded and rupture. The gauges may be provided with a solid face and a thin-plate back which is hinged to swing outward under a slight pressure. This is shown in Fig. 5-6. In mounting such a gauge, it is essential that this safety back be free to function as designed. In some installations, the gauges are mounted so that they are read indirectly by a system of mirrors. This avoids subjecting the operator to direct exposure.

The movable end of the Bourdon tube may be equipped with suitable electric contacts and used as a pressure controller. Gauges are available equipped with two such contacts, adjustable from the outside, to serve as minimum- and maximum-pressure control units. For especially precise work, the pointer may be dispensed with, and the position of the free end of the tube may be read with a cathetometer.

A gauge operating on a somewhat similar principal has been developed for pressures up to 100,000 psi. In this case, the deflecting element consists of an alloy-steel straight tube with an eccentric hole bored through it. The tube is wire-wound and heat-treated. An increase in pressure causes the straight tube to assume a curved shape, and this movement is transmitted to a dial gauge.

Piezoelectric Gauge. It was observed in 1880 by the Curies that some crystals, when subjected to a compressive force in the direction of their electric axis and normal to the faces, liberate a quantity of electricity at the faces which is proportional to the force applied. Thin plates of quartz with plane parallel faces are cut from a quartz crystal so that the plane of the faces is perpendicular to an electric axis of the crystal. These plates are stacked with alternate positive and negative faces adjacent to one another and are separated by thin metal plates somewhat like a condenser. Karcher⁹ has subjected such a stack of quartz plates to pressures as high as 50,000 psi and found that the linear relationship between charge and pressure is valid with an error of approximately 0.1 per cent. This piezoelectric effect in quartz is not present when the plates are exposed to a uniform hydrostatic pressure. The plates must, therefore, be enclosed in a gastight container, and the pressure is applied by a piston. This type of gauge is especially useful in following accurately very rapid changes in pressure. The indicating effect does not depend on the displacement of the element, and thus inertial effects are largely eliminated. When such inertia or friction effects are found in the gauge, they are due to its design and are not inherent in the principle of the gauge. This principle is not applicable to the measurement of a steady pressure.

⁹ J. C. Karcher, *Natl. Bur. Standards Sci. Paper*, **18**(445):257 (1922).

A gauge of this type is described by Edwards.¹⁰ It has been calibrated for pressures up to 100,000 psi and has a natural frequency of 85,000 cycles/sec for use in measuring a transient pressure.

Pressure-strain Gauge. Sensitive strain gauges are used extensively to measure strain in structural members. The gauge depends on the variation in electric resistance of a wire with strain in the wire. The strain gauge has been applied to the measurement of pressure.¹¹ Such a gauge is shown in Fig. 5-8. A hollow cylinder is carefully designed so that the outer circumference is strained appreciably when pressure is applied inside the cylinder. An electric-resistance winding is placed around the cylinder and is calibrated to indicate the internal pressure. The pressure-measuring element can be located very close to the pressurized container and avoids the time lag associated with long fluid-filled tubes connected to hydraulically operated gauges. The pressure is indicated by an electric instrument, and this avoids exposing the operator to the hazards of a high-pressure gauge. The Model P10 Gauge Pressure Transducer^{11a} is a different design based on a similar principle for measuring pressures up to 10,000 psig.

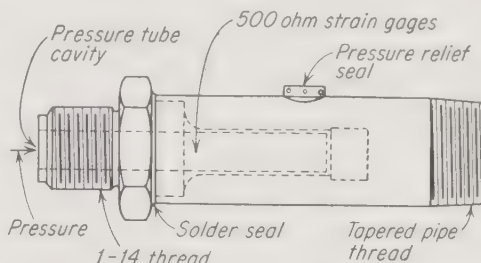


FIG. 5-8. Pressure-strain gauge. (Baldwin-Lima-Hamilton Corporation.)

Electric-resistance Gauges. The change in electric resistance of a wire with pressure may be used to measure the pressure. This was suggested by Lisell, who found that the resistance of *manganin* increased linearly with pressure. Manganin is an alloy consisting of 80 to 84 per cent copper, 4 to 5 per cent manganese, up to 12 per cent nickel, and the rest iron. This type of gauge has been developed by Bridgman,¹² who determined that the linear relationship between resistance and pressure holds up to a pressure of 13,000 atm. This gauge has been used to measure hydrostatic pressures up to 21,000 atm by extrapolating the linear relationship.

A coil of 0.005-in.-diameter silk-covered manganin wire, about 5 m long with a resistance of 120 ohms, was used for this gauge. The wire

¹⁰ P. L. Edwards, A High-speed High-pressure Gauge, *Navord* 2380 (1952) and 3963 (1955), U.S. Naval Ordnance Laboratory, White Oak, Md.; see also footnote 10a.

^{10a} R. T. Eckenrode and H. A. Kirshner, *Rev. Sci. Instr.*, **25**(1):33 (1954).

¹¹ Baldwin-Lima-Hamilton Corporation Bull. 306 and 4107, Philadelphia, Pa.

^{11a} Statham Laboratories, Inc., Bull. P10, Los Angeles, Calif., 1955.

¹² P. W. Bridgman, "The Physics of High Pressure," George Bell & Sons, Ltd., London, 1949.

is wound noninductively into a hollow ball of about 1 cm diameter. This coil is aged at 140°C for 6 to 10 hr before being used. Since the properties of manganin wire vary somewhat when obtained from different sources, each gauge must be separately calibrated.

Precision experiments using manganin wire for the measurement of high pressures are made difficult by virtue of the temperature-resistance response of the manganin. The time required for this material to reach thermal equilibrium after rapid pressure changes in the system makes manganin generally unsuited for uses in industrial-control applications.

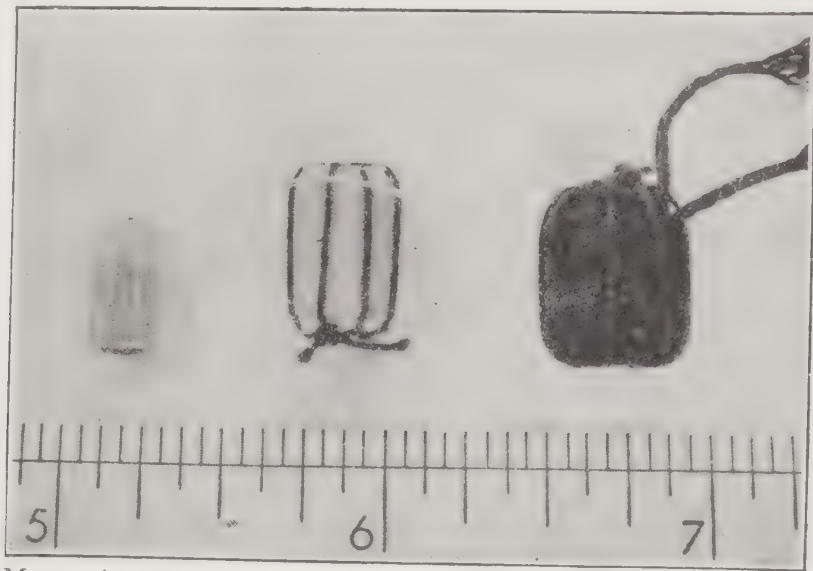


FIG. 5-9. Manganin and gold-chrome coils. [From H. E. Darling and D. H. Newhall, *Trans. ASME*, **75**:311 (1953).]

An alloy of 2.1 per cent *chromium in gold*¹³ has much less sensitivity to temperature, varying from +1 to -1 ppm/°F over the range 40 to 200°F, while manganin varies from +5 to -40 ppm in this same interval. This alloy also has a strong pressure coefficient. Typical values are 0.67 to 0.72×10^{-7} ohm/(ohm)(psi) for gold chrome as compared to 1.69 to 1.72×10^{-7} ohm/(ohm)(psi) for the manganin tested. Although the pressure sensitivity is only 33 per cent of that of manganin, gold-chromium wire has properties which make it particularly suitable for a pressure-sensing element for industrial purposes. It responds rapidly to pressure changes, it has a high degree of discrimination between temperature and pressure effects, it has adequate pressure-resistance sensitivity, and material with a high degree of uniformity is available.

Carefully selected manganin wire of 38 gauge with double-silk and double-silk plus nylon-braid insulation was wound noninductively in coils of 60 to 120 ohms resistance. These coils were stabilized by using the

¹³ H. E. Darling and D. H. Newhall, *Trans. ASME*, **75**:311 (1953).

Bridgman cycle.¹³ This cycle consisted of exposing the completed coils to temperatures of -100°F for at least 2 hr and then to $+250^{\circ}\text{F}$ for at least 8 hr and repeating this treatment several times followed by several applications of pressure above the operating range. Gold-chrome coils were wound in like fashion of 36-gauge wire. These were stabilized by baking at 300°F for at least 36 hr. Pressure-seasoning was accomplished by a single application of pressure. Finished manganin and gold-chrome coils are shown in Fig. 5-9, and a 150,000-psi pressure gauge is shown in Fig. 5-10.

Differential-pressure Gauges. The determination of instantaneous gas or liquid flow rate at high pressure requires the measurement of small

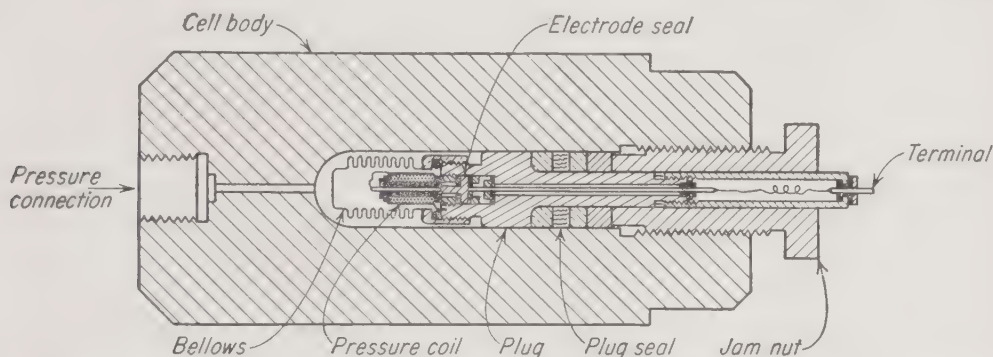


FIG. 5-10. Assembly of 150,000-psi gold-chrome pressure cell. [From H. E. Darling and D. H. Newhall, *Trans. ASME*, **75**:311 (1953).]

pressure differences. These small differences are more difficult to determine in the presence of a high absolute pressure. The instruments used for this purpose are usually either mercury manometers or a diaphragm-or bellows-type gauge. The principal problem in the design is to indicate the level of the mercury or the movement of the diaphragm or bellows with sufficient precision in a completely enclosed system. A number of designs have been used for doing this, and some of these will be described.

In Fig. 5-11a is shown a mercury manometer with a float which raises or lowers a magnetic armature *C* and actuates an induction coil *E*.¹⁴ The limitations of this design are connected with the operation of the float in a medium of varying density and with the electrical design, but it may be used at pressures up to 1,000 atm. Only the electric connections must be attached to the manometer in these units, so the pressure indicator may be placed at a distance from the flowmeter.

In the design for low pressure shown in Fig. 5-11b a number of contact points are arranged above the mercury level. Electric resistances are

¹⁴ Catalog 2008-R, Brown Instrument Division, Minneapolis-Honeywell Regulator Company, 1946.

connected between each of these contact points, and, as the mercury rises, these are shorted out progressively.¹⁵ The resistances are such that the current increases as the square root of the rise in mercury and thus directly as the flow rate. In this way, an ammeter may be used

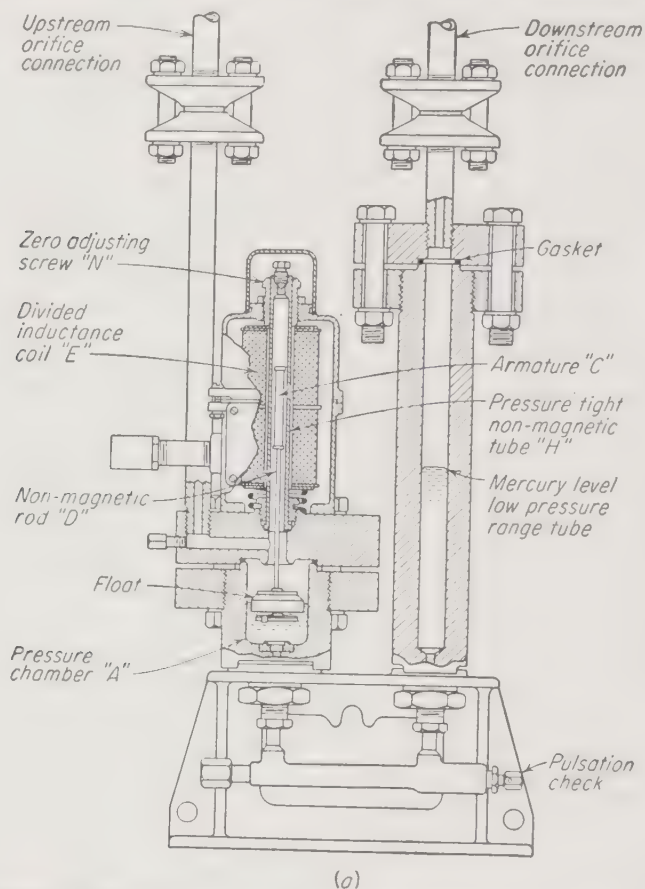


FIG. 5-11. Differential-pressure gauges. (a) Brown electric flowmeter. (Minneapolis-Honeywell Regulator Company.) (b) Republic flowmeter. (Republic Flow Meter Company.) (c) Mercury level indicated by resistance wire. (From H. Tongue, "Design and Construction of High Pressure Plant," Chapman & Hall, Ltd., London, 1934.) (d) Bosch flowmeter. (From J. H. Perry, editor, "Chemical Engineers' Handbook," 3rd ed., McGraw-Hill Book Company, Inc., 1950.) (e) Differential diaphragm manometer for pressures up to 400 atm. [From D. M. Newitt and S. K. Sirkar, *Trans. Inst. Chem. Engrs. (London)*, **9**:63 (1931).] (f) Foxboro-bellows-type differential-pressure gauge. [From W. H. Howe, *Instrument Soc. Am. J.*, **2**:109 (1955).]

as a flow indicator and a watthour meter as an integrator. For experimental work, Boyd¹⁶ has designed a manometer which uses a single contact point. This is raised or lowered by a screw through a suitable packing gland, and its height is measured by a micrometer with an accuracy of 0.001 in. In these manometers, the mercury must be main-

¹⁵ T. C. Poulter, *Phys. Rev.*, **35**:297 (1930).

¹⁶ J. H. Boyd, Jr., *J. ACS*, **52**:5102 (1930).

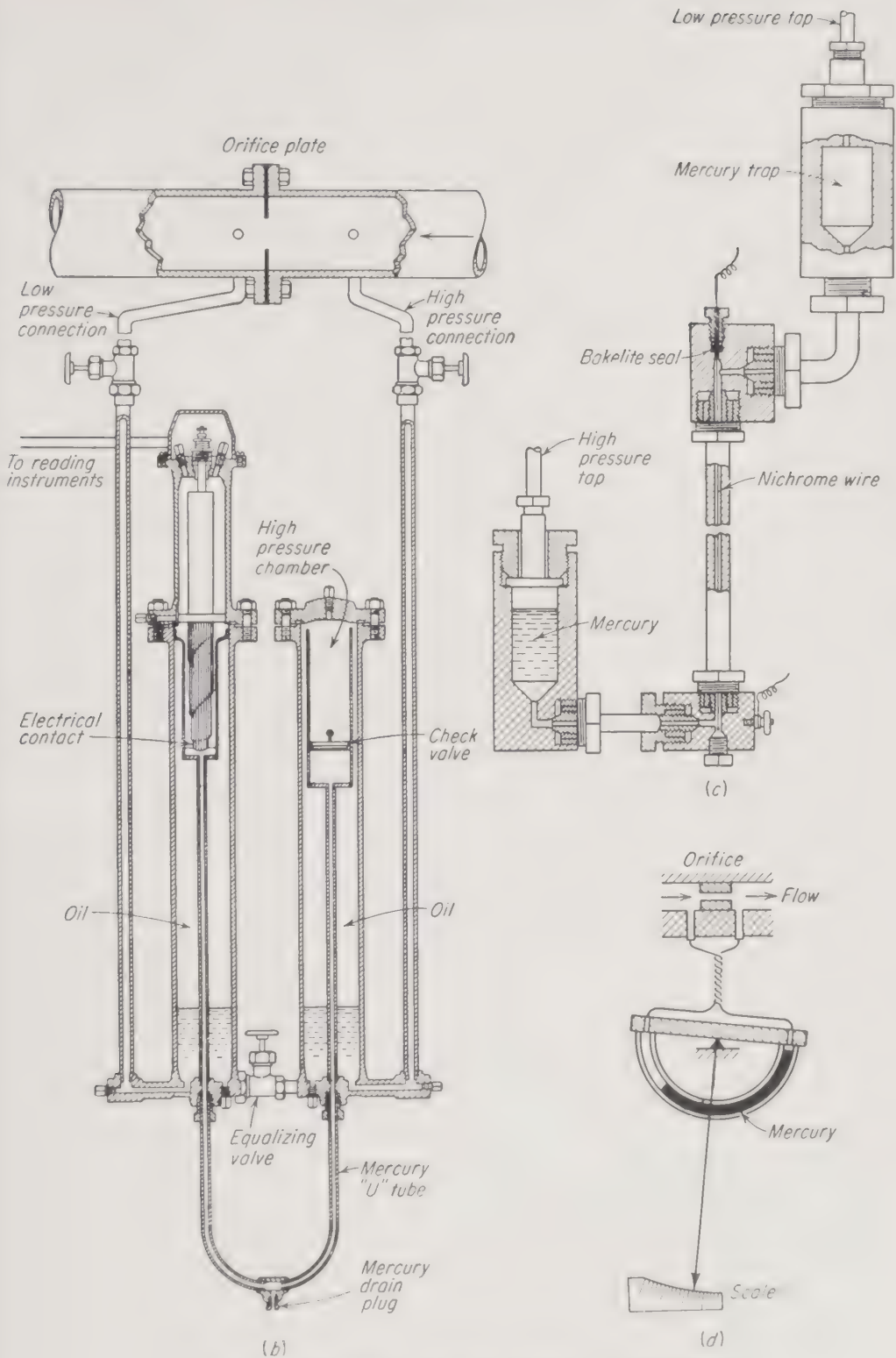


FIG. 5-11. Differential-pressure gauges. (Continued)

tained clean in order to obtain a sharp make and break with the electric contact. Another electrical method for determining the height of the mercury is shown in Fig. 5-11c. In this design a nichrome resistance wire is stretched taut through one arm of the manometer. As the mercury rises, part of this resistance is progressively shorted out, and the gauge may be calibrated to read rate of flow when readings are obtained

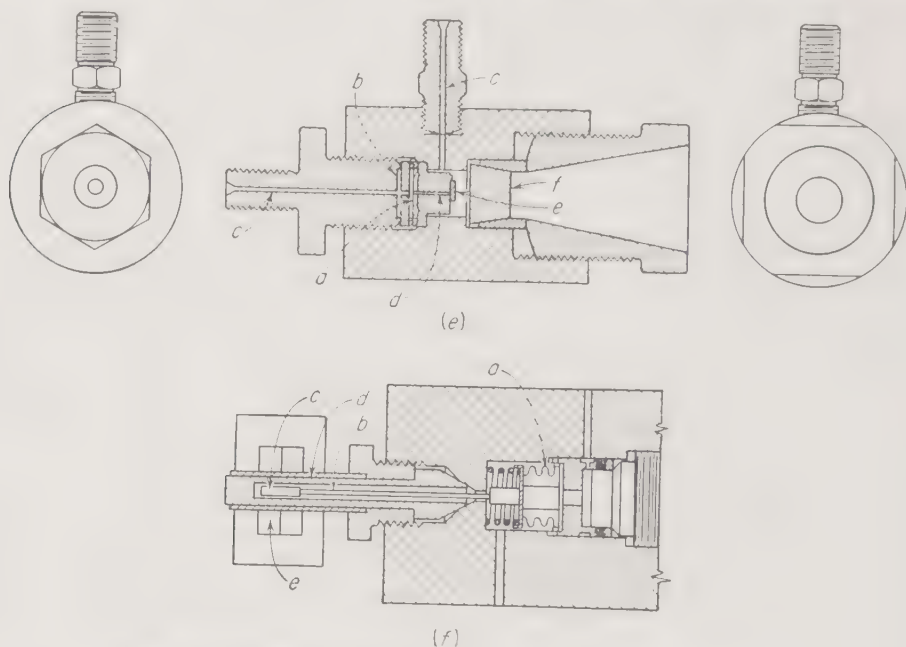


FIG. 5-11. Differential-pressure gauges. (Continued)

on a microammeter. This gauge has been used successfully for a period of time, although it is essential that the mercury be kept clean. Mercury drops adhering to the resistance wire, and other forms of surface contamination, will change the calibration. In Fig. 5-11d, a mercury manometer is constructed in the form of a semicircle with the pressure leads brought in through a very-small-diameter tubing in the form of a coil.¹⁷ This manometer is free to swing and is balanced on a fulcrum so that, when the mercury rises in one arm, it changes position and indicates by a pointer (see Chap. 4 for hazardous compounds formed by mercury and ammonia).

The diaphragm type of differential gauge¹⁸ is shown in Fig. 5-11c. Here a thin diaphragm *a* is held in a suitable pressure chamber *b*, and the pressure leads *c* are connected to the spaces on the opposite sides of the diaphragm. The center of the diaphragm is connected by a small rod *d* to a pivoted mirror *e*. The movement of the diaphragm, due to the difference in pressure on its two faces, causes a slight movement of the

¹⁷ Carl Bosch, *Chem. Fabrik*, **6**:127 (1933).

¹⁸ D. M. Newitt and S. K. Sirkar, *Trans. Inst. Chem. Engrs. (London)*, **9**:63 (1931).

mirror. The manometer is provided with a high-pressure-type window *f*, and a light beam passes through this window and is reflected from the mirror. The light beam passing out through the window indicates on a scale, and considerable magnification of the movements of the mirror can be obtained by adjusting the length of the optical system.

A bellows type of differential-pressure gauge has been developed by the Foxboro Company¹⁹ and is shown in Fig. 5-11*f*. A bellows *a* is contained in a cavity in a high-strength forging. Low- and high-pressure connections are provided to the inside and outside of the bellows. The movement of the bellows is transmitted by a rod *b* to a ferromagnetic slug *c* which moves inside a stainless-steel tube *d*. The twin coils *e* outside the tube detect the motion of the slug. The minimum slug motion should be at least 0.010 in. Units have been built which will handle a total pressure of as much as 50,000 psi and a differential pressure from 500 psi to as low as 25 psi for full-scale operation.

5-2. Closures and Connections. The construction of high-pressure equipment for both industrial and laboratory uses requires that high-pressure tubings be connected to other tubing, to fittings, or to reaction vessels. Cylindrical vessels must be closed at both ends. In some cases, a reciprocating or rotating shaft must pass through the wall of a vessel from a low-pressure to a high-pressure region. Electric connections entering a high-pressure region must be insulated from the steel walls and sealed against the pressure. In modern practice, welded connections are used whenever feasible in permanent installations. The necessity of gaining access to the inside of high-pressure vessels and of removing certain parts of the system to the shop for maintenance requires removable closures and connections. These closures are made pressure-tight by using a compression-type gasket or seal or by applying a self-sealing principle. These principles of operation will be made clear by examples.

Compression Seals. Several types of *compression seals*²⁰ are shown in Fig. 5-12*a* to *f*. The flat-type-gasket arrangement as shown in Fig. 5-12*a* represents the most elementary form of this type of seal. The gasket is placed under sufficient compression by the bolts so that the pressure in the gasket material is greater than that in the pressure vessel. Because of the broad surfaces of the gasket, a large pressure must be applied by the bolts. This is not serious when internal pressures are low, but as the internal pressure increases, the size of the flange and bolts soon becomes excessive. This difficulty can be overcome to some extent by reducing the gasket area as in Fig. 5-12*b*. With increasing pressure, the compression in the gasket soon becomes great enough to cause the gasket to squeeze out between the flanges. The obvious answer is to confine the

¹⁹ W. H. Howe, *Instrument Soc. Am. J.*, **2**:109 (1955).

²⁰ R. Taylor, *J. Soc. Chem. Ind. (London)*, **56T**(42): (February, 1937).

gasket in an inclosure. Such a design is shown in Fig. 5-12*c*. The gasket then becomes wedged in its slot and is difficult to replace without damaging the machined surfaces of the slot. The stepped-gasket enclosure shown in Fig. 5-12*d* provides a design which facilitates replacement of the gasket. This principle leads naturally to smaller and smaller gasket areas with the knife-edge or line-contact seal as the ultimate.

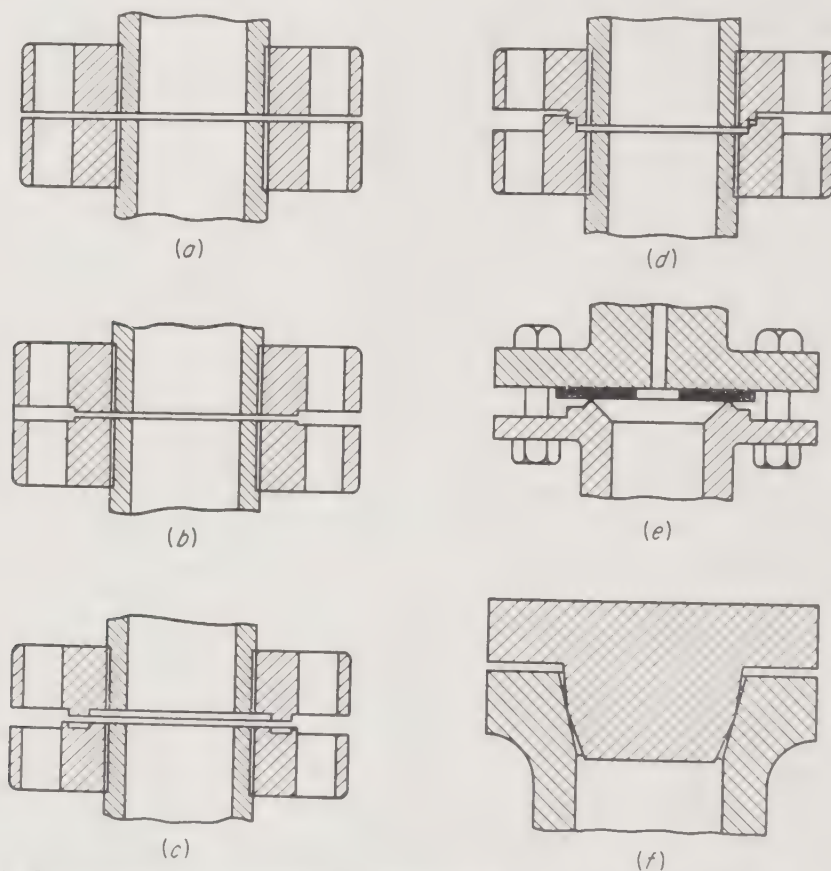


FIG. 5-12. Compression-type gaskets. [From R. Taylor, *J. Soc. Chem. Ind. (London)*, **56T**(42): (February, 1937).] (a) to (d) Gasketed, flanged connections. (e) Ipatieff knife-edge closure. (f) Line-contact seal.

The knife-edge type as in Fig. 5-12*e* has been used by Ipatieff,²¹ and the line-contact seal²² is in use in many designs. The line contact is obtained in the design shown in Fig. 5-12*f* by using two cones with 59 and 60° cone angles. These angles are not critical provided a good line of contact is obtained. It is scarcely possible to machine the sealing faces to concentrate the bolt pressure on a thin line of contact. Distortion of the metal results in contact along a line of some width. In all these seals, the initial pressure applied to the seal by bolts or screws must exceed

²¹ V. Ipatieff, *Ber.*, **37**:2961 (1904).

²² F. Haber and R. LeRossignol, *Elektrochem. Z.*, **14**:181 (1908); *ibid.*, **19**:58 (1913).

that of the highest pressure to be confined. The closures are not self-sealing. When the internal pressure exceeds the pressure in the seal, leakage is likely to occur by causing the gasket or edge to contract and shrink away from the region in which the seal is formed. The compression-type seal can be used at pressures up to several thousand atmospheres in small-size closures.

Self-sealing Designs. A self-sealing packing design has been developed by Bridgman.¹² In this design, the gasket need not be subjected to an initial pressure higher than the internal pressure which it is to seal. This design is shown in Fig. 5-13a. The total force acting on the packing is the product of the pressure inside the vessel and the cross section at the end of the disk *c* underneath the gasket. This force must be balanced by the pressure in the gasket *e* times the area of the gasket. If the area of the gasket is smaller than the area of the pressure disk under it, then the pressure in the gasket is at all times greater than that in the vessel. This is the situation in the design shown, since part of the central area of the pressure disk is unsupported. This unsupported area results in a higher pressure in the gasket than in the vessel. The gasket material is always under a higher pressure than that in the vessel, and leakage cannot occur. On the other hand, clearances must be small or the gaskets will be extruded either into or out of the vessel. At extremely high pressures, special metal rings can be used to avoid extrusion of the gasket. At ordinary temperatures, the limit to the pressures which can be held by this closure is set by the strength of the metal itself. This limitation is due largely to a pinching-off effect in the central column above the unsupported area, as the pressure in the packing increases. The pressure in the gasket is a hydrostatic pressure and acts equally in a radial direction and in the axial direction, tending to pinch off this column and eject it. At ordinary temperatures, soft rubber is a convenient packing material. At higher temperatures, lead and other soft metals are used. The hard ring *d* provides a bearing surface for the nut *b*.

Another type of partially self-sealing closure employing line contact is the lens ring²³ shown in Fig. 5-13b. A carefully machined metal ring fits into a cone-shaped space, and the initial seal is made by pushing the sides of the cone together. As the internal pressure increases, it acts on the inside of the ring and forces it against the edge of the cone. At pressures as high as 3,000 atm the lens ring is satisfactory only for small vessels up to 1 in. in diameter.

The ring²⁴ *a* shown in Fig. 5-13c requires only that dimension *X* be about 0.002 in. less than the opening into which it fits and that the

²³ F. H. Bramwell, U.S. patent 1,722,623.

²⁴ A. M. Whitehouse, P. L. Golden, R. W. Hiteshue, and E. L. Clark, *Chem. Eng. Progr.*, **49**:491 (1953).

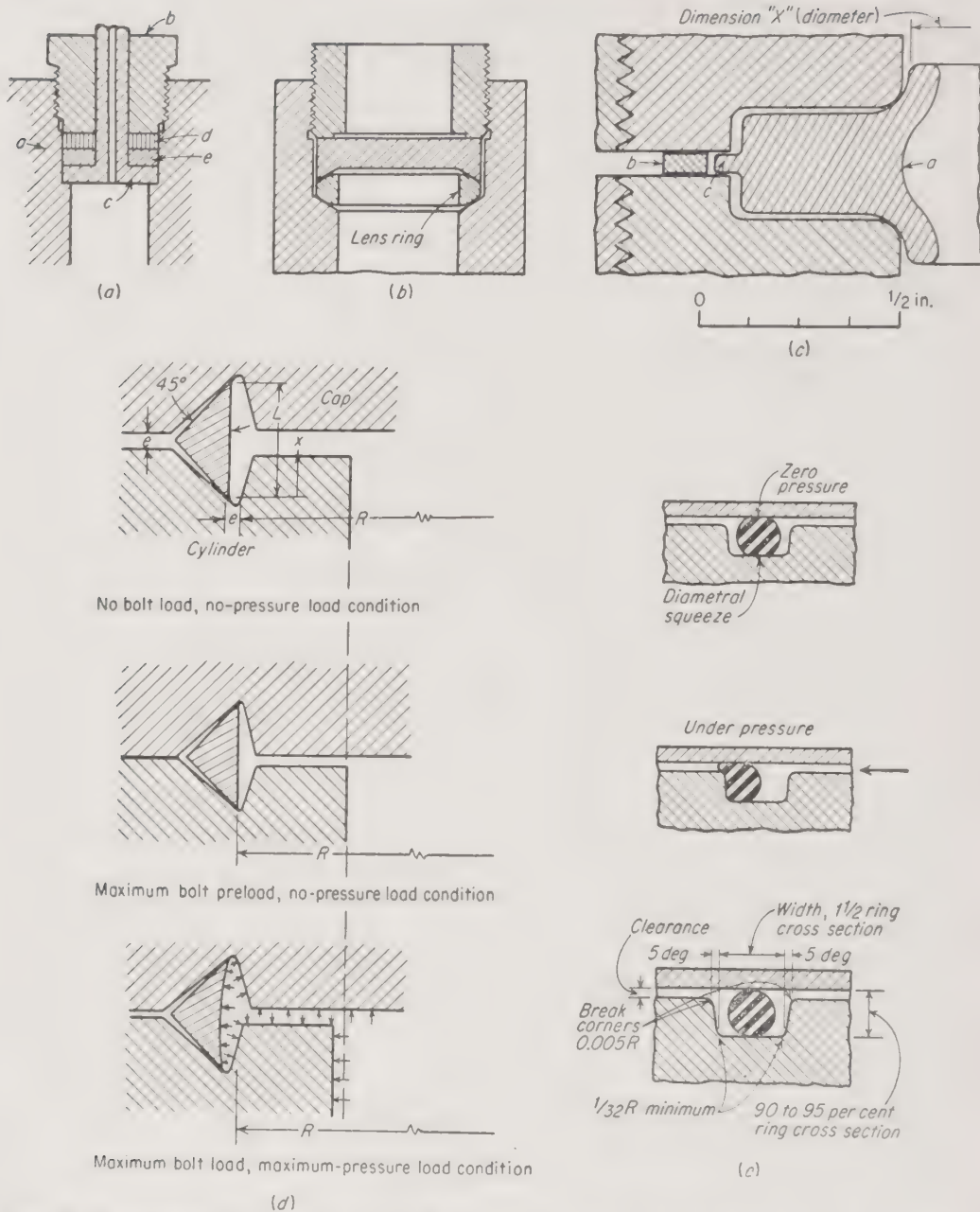


FIG. 5-13. Self-sealing gaskets. (a) Bridgman unsupported-area packing. (b) Lens ring. (F. H. Bramwell.²³) (c) Modified lens ring. [From A. M. Whitehouse, P. L. Golden, R. W. Hiteshue, and E. L. Clark, *Chem. Eng. Progr.*, **49**:491 (1953).] (d) Δ-ring gasket. [From B. A. Niemeier, *Trans. ASME*, **75**:371 (1953).] (e) O-ring gasket. (Precision Rubber Products Corporation.)

surfaces which contact each other be polished. The indicated radii are not critical, since the relationship between the mating concave and convex surfaces is determined when the vessel is fitted for hydrostatic testing; a shim b of the proper thickness is then fabricated. Forming the initial seal requires very little force, and permanent deformation is avoided. As the pressure increases, the load on the sealing surface increases; but the radii of the mating surfaces afford a rapid increase in contact surface, thereby keeping the compressive load within the elastic limit. The ring can follow movement of the head due to normal bolt strain. The small ring c projecting from the main body of the sealing ring a provides a means of minimizing misalignment of the axis of the sealing ring with the axis of the vessel. This projection and the general shape of the ring (which assures alignment) avoid one of the difficulties of the lens ring.

A design of self-sealing closure for large vessels is the Δ ring, or wedge-type gasket, shown in Fig. 5-13*d*. The gasket is self-sealing and easily removed. Niemeier²⁵ states:

The ring is a wedge that the pressure drives into a cavity provided by the cap and body. Galling does not happen when the cap-cylinder angle is less than the ring angle by an amount only slightly less than the angle of repose, and the following formula is used to determine the width of the ring

$$L = \sqrt{\frac{d^2 p_1}{E[\tan(45 + \frac{1}{2} \arctan f) - 1]}} \quad (5-6)$$

The triangular ring stretches, [as] a thin-wall cylinder, for as the pressure is applied the cap lifts away. The outer cavity angle may be defined in terms of the radial increase in the gasket

$$\tan(45 + \frac{1}{2} \arctan f) = \frac{\Delta r + x}{x} \quad (5-7)$$

The radial displacement for a thin vessel, such as this ring, depends on the internal pressure and takes the form

$$\Delta r = \frac{pr^2}{Et} \quad (5-8)$$

The thickness t , of the axial element x units long, has a value $x/2$, but one end, $x = 0$, remains fixed and thus we can write

$$2\Delta r = \frac{2pr^2}{Ex} \quad (5-9)$$

[Eq. (5-9)] combined with [Eq. (5-7)] gives

$$\tan(45 + \frac{1}{2} \arctan f) = \frac{pr^2}{Ex^2} + 1 \quad (5-10)$$

²⁵ B. A. Niemeier, *Trans. ASME*, **75**:371 (1953).

The maximum value x is, by the limits imposed by [Eq. (5-7)], $L/2$. With this value [Eq. (5-10)] can be transformed to give the axial length of [Eq. (5-6)].

A type of self-sealing gasket of simple design is shown in Fig. 5-13e. The gasket is an O ring made in the form of a rubber or composition ring or doughnut molded and trimmed to close tolerances with a round cross section. This seal was invented by N. A. Christensen [U.S. Patent 2,281,138 (1942)]. A carefully dimensioned groove or slot is provided for the O ring,²⁶ and the two surfaces to be sealed are brought together so that the distance between them is about nine-tenths of the diameter of the O-ring cross section. This produces a diametral squeeze which provides for the initial sealing. Under pressure, the internal pressure forces the O ring to one side and into the small space between the edge of the groove and the other surface. Pressures as high as 60,000 psi have been sealed in this way under static conditions.

The design of permanent and removable closures for cylindrical vessels will be described, and the application of the above sealing principles will be applied to them. This discussion will largely follow the classification of closures by Meigs.²⁷ The type of closure for the end of a vessel depends upon the frequency of opening, the size of the vessel, the temperature and corrosive conditions under which it will be used, the connections which must pass through the end of the vessel, and the type of access provided by the removable head.

Permanent Closures. Several types of permanent closures are shown in Fig. 5-14a to e. A convenient type of vessel is constructed by boring out a solid rod and leaving a substantial end as a closure as in Fig. 5-14a. For laboratory research, this shape of end is suitable for use with a can type of liner made of Pyrex, nickel, silver, copper, or stainless alloy. At pressures above 50,000 psi, the inside corners should be rounded and provided with a fillet. A formed end as in Fig. 5-14b can be obtained by forging or casting. This shape is formed from a solid ingot by not forcing the piercing tool all the way through. Equipment for hollow forging is costly, and this design is limited to standard sizes in production quantities. For pressures below 5,000 to 10,000 psi, this design may be formed from a heavy tube by nosing or swaging one end closed. A simple and inexpensive design is shown in Fig. 5-14c using a welded flat disk. The diameter to which this design may be applied is limited by the inefficient stress distribution in a flat plate. For larger vessels, the stress distribution can be greatly improved by using a formed cap butt-welded to the sides of the vessel as in Fig. 5-14d. Formed welding caps for this purpose are available in standard sizes of heavy pipe for pressures

²⁶ Precision Rubber Products Corporation, "Handbook of O-ring and Dyna-seal Packings," Dayton, Ohio, 1953.

²⁷ D. Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**:769 (1943).

up to 1,000 or 2,000 psi. When especially designed, the welded cap may be used at pressures up to 6,000 psi and in sizes up to several feet in diameter. The thickness of the wall is limited by the thickness of weld which can be successfully formed. This is about 6 in. The threaded plug is another variation of closure as shown in Fig. 5-14e for small vessels. This is screwed in and welded. In this case, the end thrust is carried on machine threads, and the weld serves to make the joint gas-tight. This design is not so well adapted to absorbing the stress concentration which develops when the cylinder walls are overstressed.

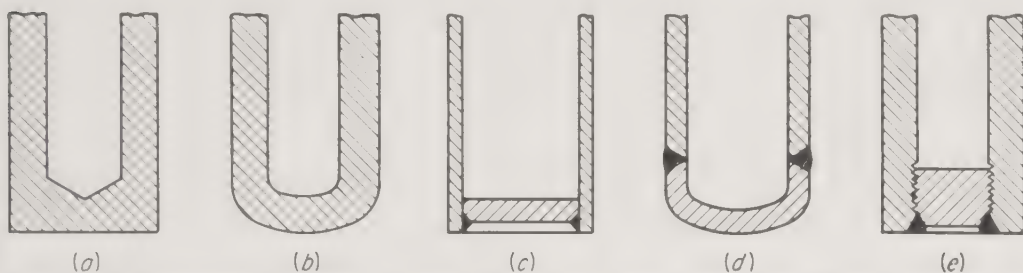


FIG. 5-14. Permanent closures. [From D. Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**: 769 (1943).] (a) Solid bored end. (b) Solid forged end. (c) Welded flat disk. (d) Butt-welded preformed cap. (e) Screwed plug, welded.

Removable Closures. When the closure is to be opened only occasionally, the time and effort involved in opening it are not of serious consequence. Some of the factors to be considered in connection with the ease of removal are the weight of the metal flanges, the number and size of the bolts used, the tendency to score or deform the sealing faces, the length and weight of tools required for opening the closure, the amount of insulation and auxiliary construction which must be removed from around the bolting flanges, and the cost of the gaskets which are replaced. When the closure is to be opened frequently, it is desirable to provide the following:

1. Light-weight removable parts
2. A design of bolt closure which requires that bolts be only loosened and not removed
3. Sealing faces which are pressed tight to avoid turning one sealing face against another and scoring the faces
4. Elastic sealing faces as in lens rings
5. A closure designed for use with tools of a comfortable and convenient size

Flanged Closures. Bolted flanges are probably the oldest method of providing a removable closure for a pressure vessel. Two examples of these are shown in Fig. 5-15a and b. In the first of these, the gasket is confined between male and female faces. One of the pair of flanges is

butt-welded to the opening in the vessel. This type of flange is well standardized and requires little machine work in its fabrication. It is not well suited to frequent removal, but its low initial cost adapts it to preliminary experimental work. In the second method of construction, threads are cut in the outer wall of the vessel, and one of the pair of flanges is screwed to these. The gasket is confined in a groove cut in

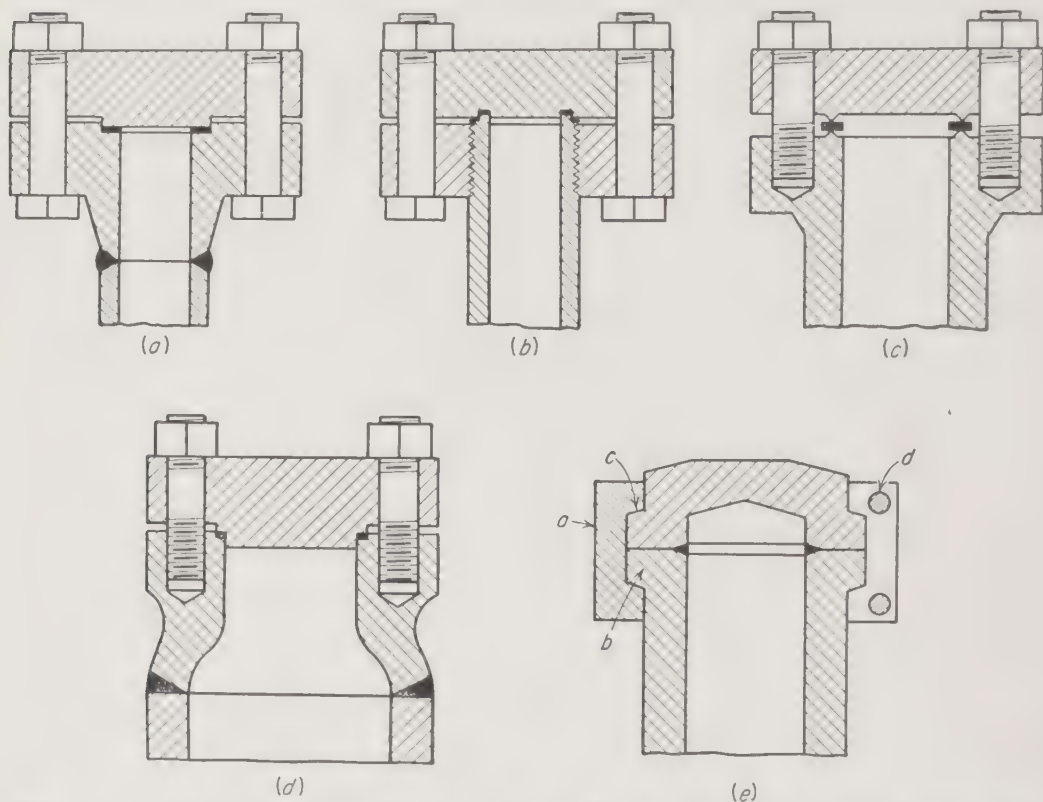


FIG. 5-15. Flanged closures. [From D. Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**: 769 (1943).] (a) Bolted flange, welded. (b) Bolted flange, screwed. (c) Ipatieff closure. (d) Flange neck, welded. (e) Vickers-Anderson joint.

the face of the other flange with a tongue turned in the end of the vessel wall. In Fig. 5-15c the flange on the vessel is forged integrally with the body, and the Ipatieff²¹ type of closure is used. The outer diameter of the flange circle is reduced by forging the flange as an integral part of the wall, and this also reduces the required thickness of the flange. This type of closure is expensive and, like the other flanges described, requires the complete removal of a number of bolts before the head can be taken off. However, no other type of construction makes so large an area available in the head for pipe connections, electric leads, thermometer wells, and agitator shafts. For this reason, a great majority of autoclaves for stirring at pressures up to 3,000 psi are designed with bolted-flange closures.

The large diameter of the flange-type closure can be greatly reduced by using the flange-neck closure as shown in Fig. 5-15*d*. However, this reduces the area available for connections through the head. The neck flange has the same outside diameter as the vessel and is butt-welded to the end of the cylinder. The construction is especially suitable for pressure vessels over 2 or 3 ft in diameter where the pressure exceeds about 2,000 or 3,000 psi.

The bulkiness of flange joints with their large number of bolts is greatly reduced in the Vickers-Anderson type of joint²⁸ shown in Fig. 5-15*e*. A closely fitting collar *a* made in several segments fits around the outside of the flanges *b* and carries all the tensile stress normally carried by the bolts. The segments of this collar are drawn together by tangential bolts *d*. Two narrow shoulders *c* are provided on both the body of the bomb and the closing head. The upper and lower faces of these shoulders are machined at a slight angle to the perpendicular. The supporting collar *a* bears on these shoulders, and this angle is sufficient to force the two flanges together. The internal pressure in the vessel results in a radial stress because of the angle of the faces. However, the angle is small enough so that this radial component is overcome by friction. The uniform distribution of the stresses around the periphery of the Vickers-Anderson joint results in a large reduction in the bulk of the flange joint. The tangential bolts do not carry the stresses usually carried by bolted flanges. This is of considerable importance when the diameter exceeds 2 or 3 ft at pressures over 2,000 psi. The chief disadvantage is the highly precise machine work required for the joint to make up uniformly tight.

A popular self-sealing flange closure for large heads employs the Δ -ring gasket shown in Fig. 5-13*d* and already described. The unsupported-area principle is applied in this gasket with the radial pressure being applied at the sealing surfaces in a radial direction.

Screwed Closures. Figure 5-16*a* shows a simple screwed plug with a confined gasket. This is a common type of closure for very small openings and is probably the least expensive. The closure is useful at surprisingly high pressures and, when used with a hardened lens ring as described by Newitt,²⁹ is self-sealing and will withstand pressures up to 75,000 psi. The twisting action of this type of screwed closure on the gasket is not well suited for frequent removal of the plug. When a liner is to be used in the vessel, this action also tends to damage the edges of the liner.

²⁸ Harold Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman and Hall, Ltd., London, 1934.

²⁹ D. M. Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.

These disadvantages can be remedied by a change in the design as shown in Fig. 5-16*b*. Here a threaded sleeve is provided which bears on a shoulder of the plug. The plug does not rotate and can thus be forced directly down upon the gasket. It may be opened and closed

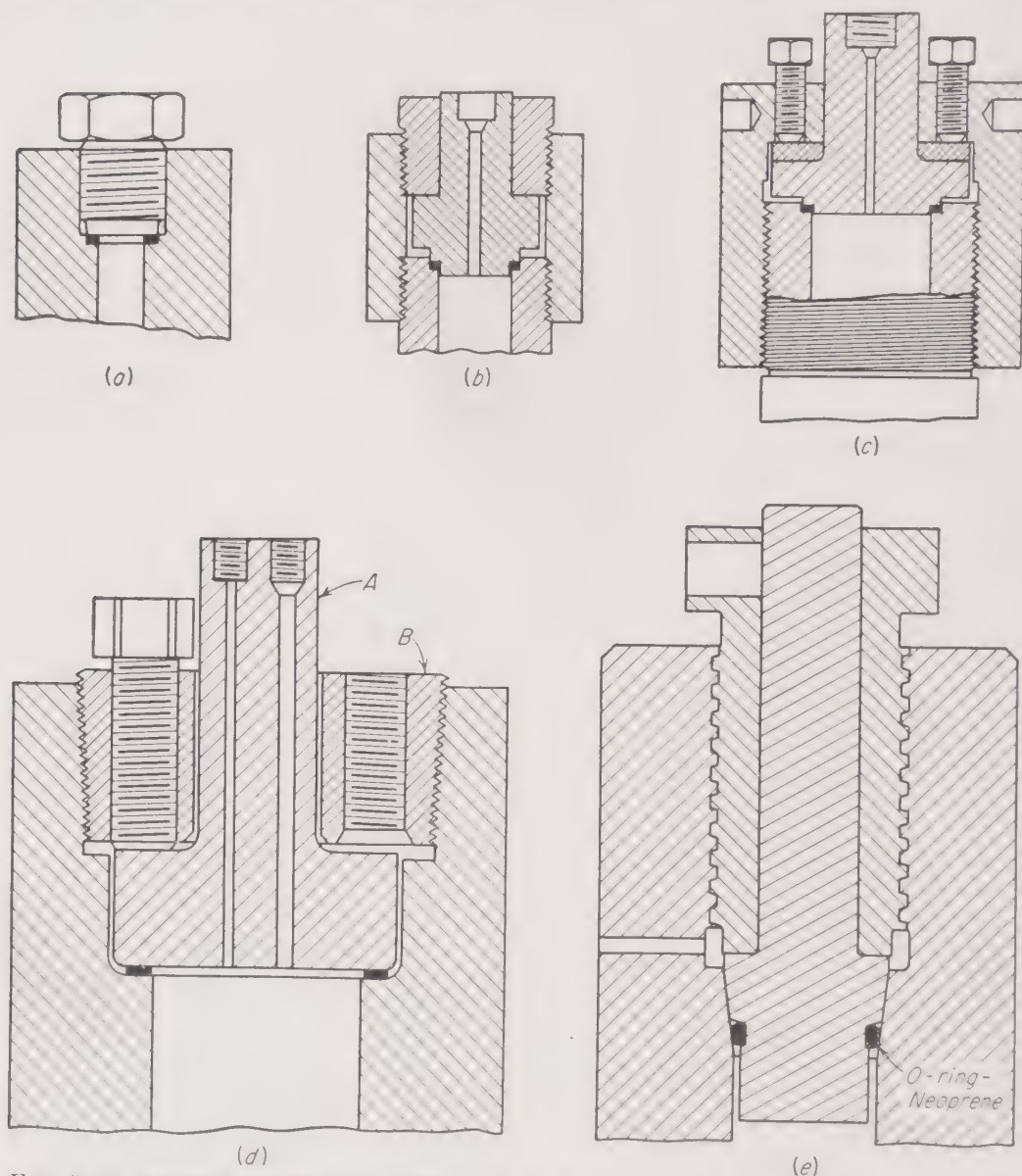


FIG. 5-16. Screwed closures. (a) Screwed plug, gasketed. [From D. Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**:769 (1943).] (b) Screwed sleeve and plug. (c) Compression head. (d) Tapered cap-ring closure. (e) O-ring closure. (*Autoclave Engineers Inc.*)

repeatedly. These two screwed closures are not suitable for large-size openings, since for openings up to 3 in. diameter a pneumatic or hydraulic vise and wrench are required. The design is suitable for pressures up to 20,000 psi in diameters up to $1\frac{1}{4}$ in. and up to 60,000 psi for smaller

openings. Where a self-sealing gasket is used for high pressures, even more force may be required to open it after use. This type of closure requires careful machining to ensure that the gasket and plug parts are coaxial with the sleeve.

A modification of the screwed compression-head closure as developed by Reynolds²⁷ is shown in Fig. 5-16c. A cap is screwed over the end of the vessel, but the threads in this cap do not provide the closure. A ring of small cap screws bears on the closing plug and provides the compression necessary to effect the seal. These cap screws need not be removed entirely, but only loosened, and then the complete head can be unscrewed. This type of closure is particularly suitable where the contents must be poured from the bomb without contaminating the head. Above diameters of 6 to 8 in., this type of closure becomes costly and bulky.

A quick-opening closure for vessels with an inside diameter of 6 to 16 in. and for pressures from 5,000 to 50,000 psi is shown in Fig. 5-16d. This is a tapered cap-ring closure provided with a tapered cap and tapered thread. With a lens-ring gasket, it is self-sealing and is one of the quickest-opening closures for this class of service. A uniform gasket pressure is provided by the ring of cap screws. When these are loosened, a few turns are sufficient to disengage the threads between the cap and body, providing easy and quick removal of the cap. These tapered threads are self-aligning and provide for rapid centering of the cap. Hardly more than a turn of each of the cap screws is then sufficient to seal the opening.

An O-ring gasketed closure for vessels with an inside diameter of 1 or 2 in. and for working pressures up to 30,000 psi is shown in Fig. 5-16e.

Where a nut slides over the surface of a fixed sleeve, this surface should be liberally lubricated with a paste of powdered graphite such as Gredag, having approximately the consistency of putty. The same mixture will minimize binding if applied to all threads and bearing surfaces when tightening pressure vessels, especially those subjected to high temperatures. Molybdenum sulfide has also been used as a thread lubricant at high temperatures. Extremely tight fits in the threads should be avoided, and the pitch of the male and female threads should be the same within very close limits. Coarse threads do not show so much tendency to gall as fine ones, but the mechanical advantage and bolt strength are in favor of the latter. The threads may be made freer by grinding them in with a fine grinding compound prior to subjecting them to great stress. A difference in the hardness of the mated parts will frequently prevent seizure.³¹

Bridgman-type Closures. Modifications of the Bridgman unsupported-area principle comprise one type of closure. This is an axial type of self-sealing closure, whereas the Δ -ring and lens-ring closures are radial types.

In the axial type, the force of the internal pressure is applied to a floating head in the direction of the hollow-cylinder axis. The head closes the end of the cylinder by applying the axial force to a soft gasket material which resolves the force by a Poisson effect into a gasket pressure acting radially. This pressure provides the seal. This action contrasts with radial types, where the internal pressure acts radially and its force is transmitted directly into radial-contact pressure by a slight stretch of the ring. The ring is then designed to undergo more elastic deformation than the related cylinder and head. Three Bridgman-type closures are shown in Fig. 5-17*a* to *c*. The first (Fig. 5-17*a*) is a simple form for use in small sizes up to 1 or 2 in. in diameter. This design is not easily opened and suffers from jamming of the gasket.

The design shown in Fig. 5-17*b* has been used extensively to seal large-diameter vessels. The floating head squeezes a somewhat triangular-shaped gasket into the space between the floating head and the vessel wall, providing an excellent seal. This closure requires a considerable amount of precise machining of large pieces in order to avoid extrusion of the soft gasket. When the gasket extrudes, it causes the closure to stick and complicates removal and replacement of the head.

Newhall³⁰ has simplified the machining and reduced extrusion of the gasket by inserting brass rings at all crevices where extrusion can occur, as recommended by Bridgman.¹² This arrangement is shown in Fig. 5-17*c*.

Information dealing with the closures of high-pressure vessels is summarized in Table 5-2.

Connections. Assembling high-pressure apparatus requires connections between tubing and tubing, tubing and high-pressure vessels, and tubing and other fittings such as valves, tees, filters, rupture safety disks, and the like. These connections are accomplished by welding, by a compression gasket, by a line contact closure between metals, or by the self-sealing principle. Typical examples will be illustrated. For connections with small tubing up to about $\frac{1}{2}$ in. OD, a common type of connection³¹ is shown in Fig. 5-18*a*. This is made by cutting a left-handed thread on the end of the tubing which is then coned to an angle of 58 or 59°. A similar female cone with an angle of 60° is provided in the body of the connection and forms a seat. A nut acts on the sleeve around the tubing and presses the two cones together, making a line contact at the joint. With tubing having an outside diameter of $\frac{1}{4}$ in., this type of joint is effective at pressures up to 100,000 psi and with $\frac{3}{8}$ -in. tubing up to 75,000 psi. Another modification of this same type is shown in Fig. 5-18*b*. This avoids cutting

³⁰ D. H. Newhall, private communication.

³¹ B. F. Dodge, in J. H. Perry, editor, "Chemical Engineers' Handbook," 3d ed., sec. 18, McGraw-Hill Book Company, Inc., 1950.

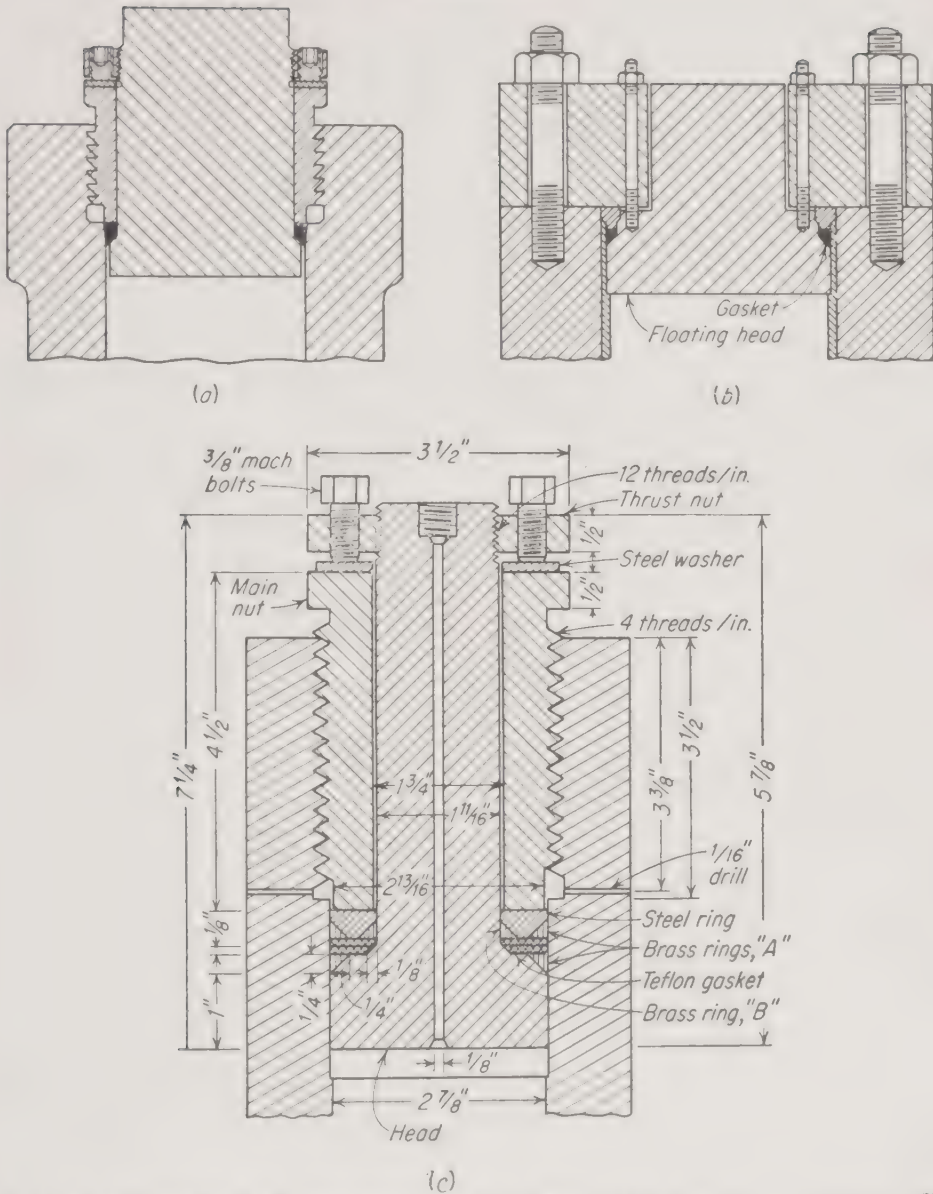


FIG. 5-17. Bridgman-type closures. (a) Bridgman-type closure. (*Autoclave Engineers Inc.*) (b) Modification for large-diameter heads. (c) Modification using rings to prevent extrusion of the gasket. (*D. H. Newhall.*)

threads in the end of the tube but requires that the cone be welded on. The seats on both of these cone-type joints may be readily refaced with a small hand reamer after they have been scored by use.

A rather compact design, which was used at the Fixed Nitrogen Research Laboratory, for joining pieces of tubing to the body of a valve or connector is shown in Fig. 5-18c.³¹ A double cone is held between the end of the piece of tubing and the body. Joints of this type have been used at pressures of 150,000 psi and more.

A compression type of gasket connection used at low pressures is shown in Fig. 5-18*d*. This uses a flat-type gasket made of lead, copper, silver, aluminum, soft iron, vulcanized fiber, or similar material. This joint is made by first threading the ends of the tubing, then facing the ends square, and cutting the gasket groove in each. The threads on one

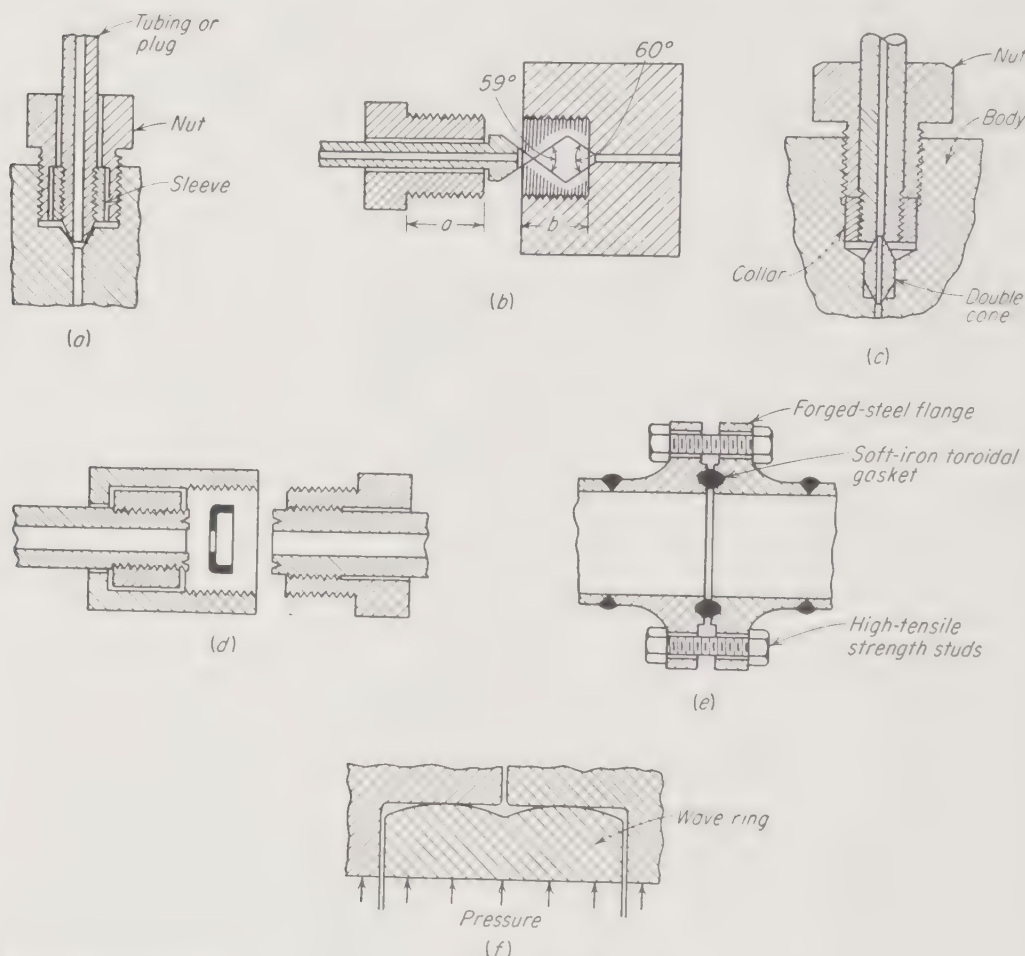


FIG. 5-18. Connections. (a) Cone turned on end of tube. (b) Cone joint. (c) Double-cone joint. (D. H. Newhall.) (d) Pressure joint. (e) Ring joint for large tubes. (f) Wave-ring pressure joint.

piece of tubing are then cut back to receive the sides of the cup gasket. The cup provides for accurate centering of the hole in the gasket and also permits assembly in a horizontal position. The gasket must be so proportioned that, when the joint is made up, a minimum pressure is provided over the sealing surface. When using copper, this pressure should be at least 60,000 psi. This is sufficient to cause the copper to flow into the gasket grooves and provide a tight seal. Gaskets $\frac{1}{32}$ to $\frac{1}{16}$ in. thick are satisfactory. The flat type of soft gasket may be replaced by harder materials as in Fig. 5-18*e*. A ring of soft iron with a diamond-

shaped cross section is suitable. The gasketed surfaces may be brought together by flanges welded to the pipe or by suitably machined parts. This design is applicable to larger sizes of joints, but flanges are usually convenient only in the standard sizes specified by the API.

A wavy-ring self-sealing type of connection is shown in Fig. 5-18f. This must be carefully designed, and both the ring and the recess provided for it must be machined to close tolerances. The internal pressure acting on the inner diameter of this ring creates a larger pressure at the two lines of contact at the outer diameter. The seal is made at the outer lines of contact. Perfect alignment is not necessary, but an interference fit is required to ensure a seal at low initial pressure.

A method of introducing a tube through the walls of a pressure vessel is described by Whitehouse, Golden, Hiteshue, and Clark.²⁴ This is a double-cone-cinch design which depends on deforming the cinch against a radius provided in the body of the fitting and is effective up to 5,000 psi. A double-cone cinch is also used in the Ermeto connection shown in Fig. 5-19. In the Ermeto design, tightening the cinch nut forces the double-cone sleeve forward, and its cutting edge shears a groove in the outer surface of the tube, giving a tight joint between the fitting and the tube. This design has been found effective up to 12,000 to 15,000 psi.

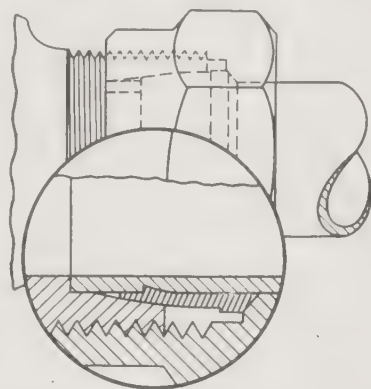


FIG. 5-19. Cone-type Ermeto fitting. (*The Weatherhead Company.*)

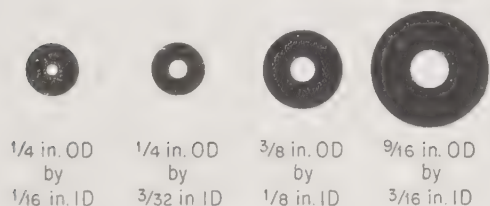


FIG. 5-20. Standard sizes of tubing.

A wide selection of tubing for handling high pressures is available. This should be seamless and cold-drawn. The tubing is usually employed to carry high internal pressures, but occasionally the high pressure may be on the external surface when it passes through a high-

pressure vessel. The pressure to which the tubing may be subjected increases as the ratio of the inside to the outside diameter decreases. This ratio becomes quite small for tubing of a small inside diameter and reasonable wall thickness, so that small tubing carries rather high pressures. The tubing may be made of steel, chrome-molybdenum steel, stainless steel, Monel metal, nickel, and other alloys. High-pressure tubing is available with an inner liner of copper for use when corrosive conditions or catalytic effects require it. A number of typical sizes of tubing are shown in Fig. 5-20, and a more complete list with the pressure range in which they are useful is included in Appendix E.

5-3. Valves. Valves for high-pressure service require careful design of the valve stem, of the packing arrangement for the valve stem, of the seat, and of safety features which are not so important at lower pressures. A small-size valve³² is shown in Fig. 5-21a. This valve can be operated at pressures up to 60,000 psi. The valve stem is nonrotating and is equipped with a hardened conical point which seats in the body of the valve. This seat may be resurfaced when worn by using a flat-bottom drill. The valve is used in laboratory applications with $\frac{1}{4}$ - to $\frac{9}{16}$ -in. OD tubing.

Another valve design³³ is shown in Fig. 5-21b. The valve stem is packed below the threaded portion, and the thrust on the threads is reduced by using a stem of smaller diameter than the threaded portion. A shoulder on the valve stem is a safety feature so that the valve stem cannot be blown out through the packing-gland nut even though the threads should be completely stripped from it. This design is for pressures up to 60,000 psi and for tubing up to $\frac{1}{2}$ in. OD. At very high pressures a means to reduce the friction in the threads on a valve stem may be desirable. To accomplish this, valves may be operated by oil- or water-driven diaphragms or pistons. Thrust bearings can be used, or the valve stem may be extended through the valve body, which then requires the use of a second packing gland.

The use of an O ring as a valve packing reduces the friction below that of the compression type of packing. Such designs, which have been used to 60,000 psi, are shown in Fig. 5-21c and e. Another self-sealing packing is shown in Fig. 5-21d. This is a Bridgman closure with rings to confine the gasket in a design by Harwood for pressures of 100,000 psi and higher. The valve seat is closed by a ball and the stem does not rotate. The valve design shown in Fig. 5-21e has a floating stem which does not rotate. This stem is pushed directly into the seat. The stem is packed with an O ring.

usually Valves used in high-pressure service must usually withstand excessively high pressure drops across the valve seat. This results in extreme velocities and severe erosion. In the valves described above, *(valves)* the valve stem is provided with a hardened conical point which forms its own seat in the softer metal of the valve body. The seat must be refaced frequently under these conditions. A valve will seat because of the turning action of the stem even when there is scale or grit present. The valve³¹ shown in Fig. 5-21f is equipped with a replaceable seat *b* provided with its own gasketed seal *c* as well as a replaceable valve-stem head *a*. The head rotates on the end of the valve stem *d* so that it does not turn in the

³² Catalog 406, American Instrument Company, Silver Spring, Md., 1955.

³³ Catalog 200, Autoclave Engineers Inc., Erie, Pa., 1953.

seat. This action avoids excessive scoring of the seat but makes it difficult to close the valve tightly when dust or grit is present. Both head and seat may be provided in a material such as Kenna metal harder than that of the main valve body.

When a valve is used in continuous commercial service, it is an advantage to be able to repack the stem without releasing the pressure in the valve. This can be accomplished in the design shown in Fig. 5-21*g*. Here the head of the valve stem is provided with a double cone. An upper seat screws in below the packing and seals against a gasket. The valve stem may be screwed out until its upper cone seats, thus closing the high-pressure region of the valve and permitting the packing to be replaced.

When a valve is to be used in relatively high-temperature service, both the packing around the valve stem and the threads which advance the valve stem should be at a somewhat lower temperature than the body of the valve. A design for accomplishing this result is shown in Fig. 5-21*h*. The valve stem *e* as well as the valve-stem housing *d* are both quite long, and the latter may be provided with a jacket for water-cooling or be fitted with fins for air-cooling. The threads are outside the packing, and both the head of the valve stem and the seat in the body are removable. The head is made in two pieces, *a* and *b*, and the upper piece is coned so that the valve may be repacked under pressure. In order to operate in this fashion, the two parts of the head must be sealed together with a gasket. The end of the valve stem is rounded slightly, providing for sufficient play to enable the head to find its seat. By removing both the valve stem and the seat *c*, the body may be welded into place without warping these critical parts.

Where a high-pressure valve is used for the automatic control of pressure, the valve stem is likely to be in continuous active motion. There is then a serious problem of providing a valve-stem packing which will have negligible leakage, low friction, and long life. The valve shown in Fig. 5-21*i* uses a novel bellows design to provide a hermetic seal without conventional packing. This bellows is shown on an automatic control valve at *a*. A section through the bellows is shown at *b*. The flexible metal bellows *c* is supported by a group of collars *d* contoured to match the bellows. These collars support the inside of each inner convolution of the bellows which is subjected to collapsing pressure. The outer convolution is then subjected to a fairly uniform tension from the internal pressure. An individual convolution is shown at *e*. A triple-walled tubing is used for greater flexibility and increased stroke. This type of bellows has been constructed to withstand 25,000 psi. With an internal pressure of 10,000 psi, they have withstood 20,000 cycles of elongation and contraction with 0.003-in. motion per convolution.

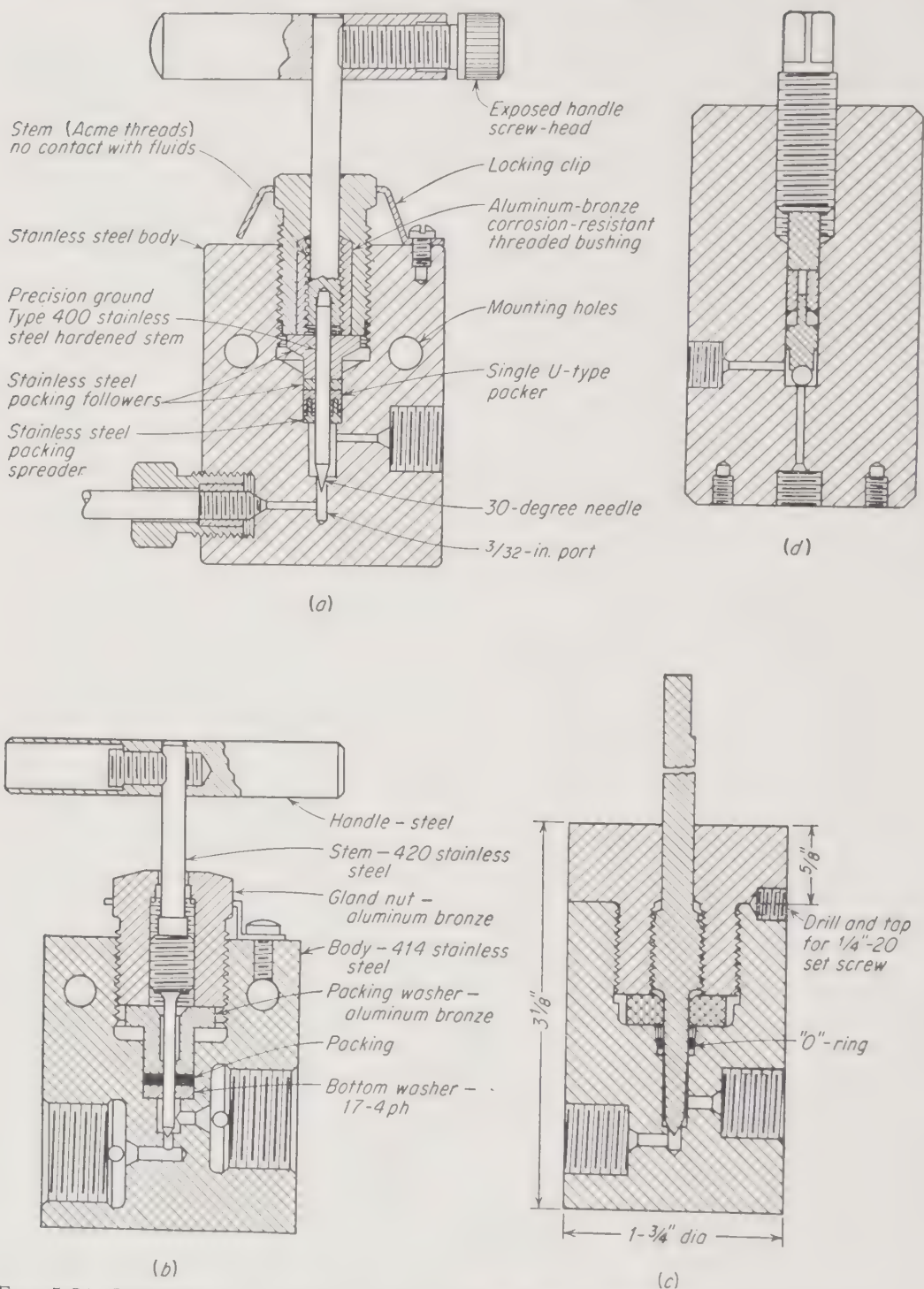
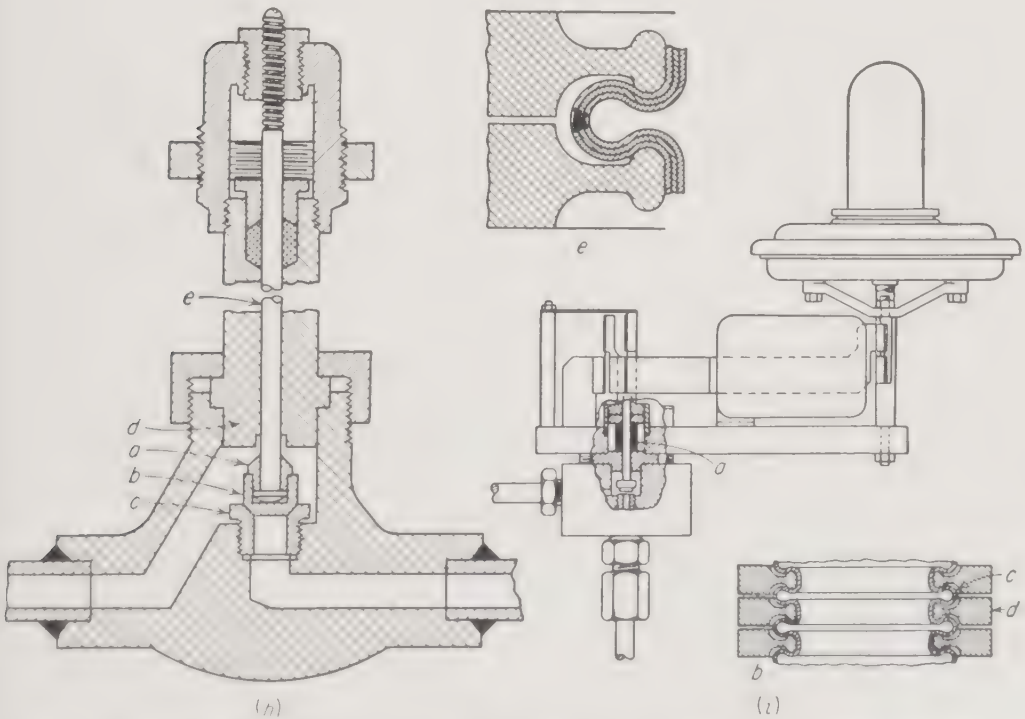
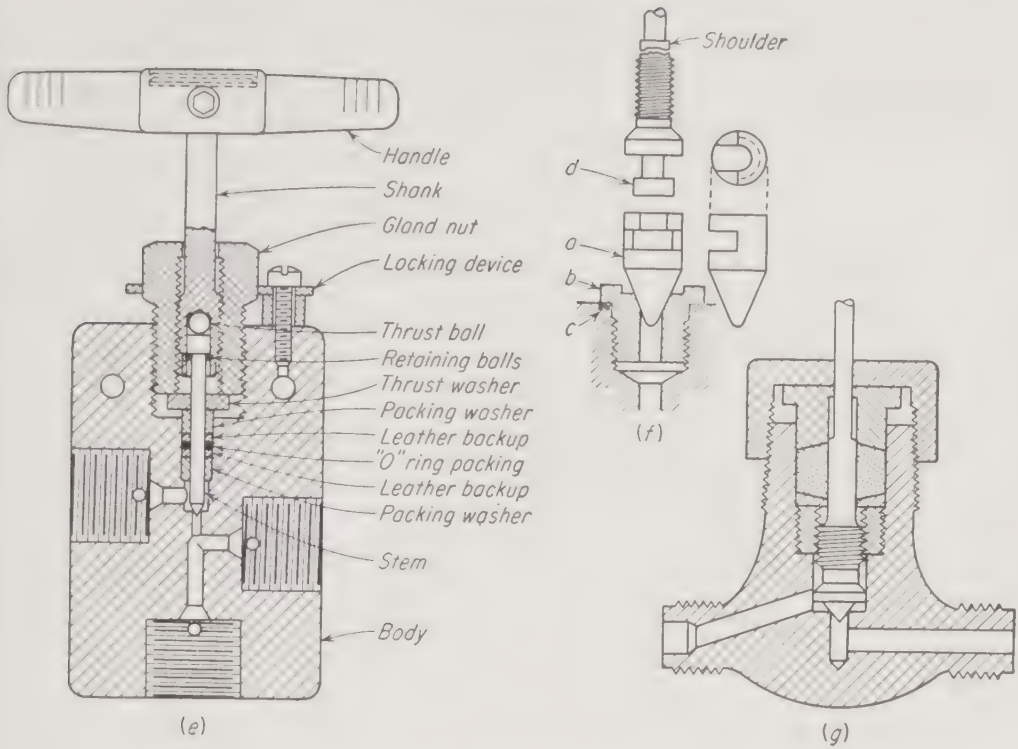


FIG. 5-21. High-pressure valves. (a) For 60,000 psi. (American Instrument Company, Inc.) (b) For 60,000 psi. (Autoclave Engineers Inc.) (c) O-ring packed valve. (From H. C. Van Ness.) (d) Harwood valve. (Harwood Engineering Company.) (e) Valve for 60,000 psi with floating nonrotating valve stem. (Pressure Products Industries, Inc., Halboro, Pa.) (f) Replaceable seat. (From "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.) (g) Forged valve for repacking under pressure. ("From Chemical Engineers' Handbook,"



3d ed., McGraw-Hill Book Company, Inc., New York, 1950.) (h) Valve for use at elevated temperatures. (From "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.) (i) Foxboro valve for automatic pressure control. [From W. H. Howe, *Instrument Soc. Am. J.*, **2**:109 (1955).]

Relief Valves. Considerable difficulty has been encountered with relief valves in designs where the valve does not reseal itself after functioning. Ernst and Reed³⁴ describe a valve which is satisfactory in this respect. It will relieve pressure thousands of times and reseal itself each time.

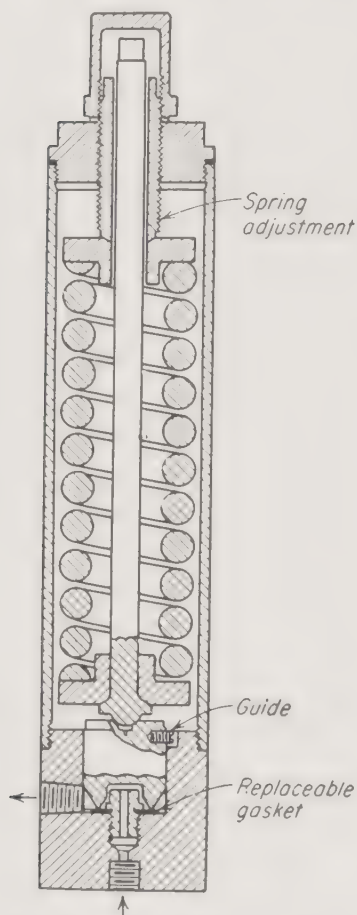


FIG. 5-22. Relief valve. [From F. A. Ernst and F. C. Reed, *Fixed Nitrogen Research Laboratory, Chem. & Met. Eng.*, **37**:580 (1930).]

This valve is shown in Fig. 5-22. The closure is made between a seat of soft material, such as copper, and a circular sealing edge which is machine ground and lapped with great care to ensure perfect contact along the edge. This sealing edge is then self-aligning, being acted upon by a spherical contact point on top of the disk. The valve can be adjusted to relieve at a given pressure over a considerable range; and by changing the dimensions the maximum and minimum pressure can also be varied appreciably. Such valves are available for pressures up to 25,000 psi (see also footnote 32). For this valve to reseal properly, the gas must be free of dust and grit. This can be ensured by inserting a copper-gauze-and-steel-wool filter in the line upstream from the valve.

Pressure Regulators. The back-pressure regulator²⁴ shown in Fig. 5-23a maintained a fixed system pressure in the range from 300 to 4,000 psi at flow rates from 0.3 to 2 cu ft/hr (STP). It is built of type-303 stainless steel except for the cap of cold-rolled steel, a hardened type-410 washer and needle, a seat insert of teflon, the neoprene diaphragm, and a music-wire spring. Clearance of the parts that retain the diaphragm must be of the order of 0.0015 to 0.005 in.

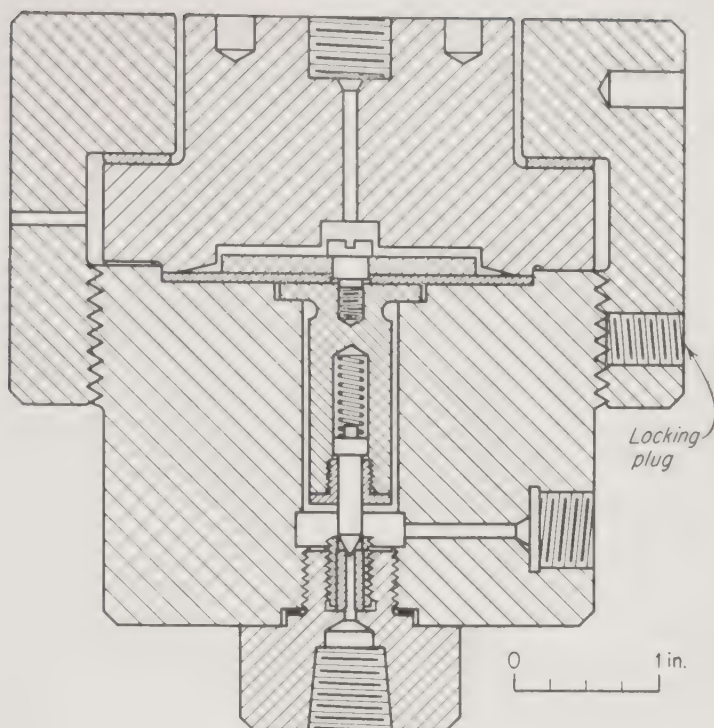
to prevent extrusion of the neoprene diaphragm. The gas must be filtered, since the smallest particle of scale or solid material will prevent proper functioning. A magnetically operated pressure-reducing valve is described by Larson and Karrer.³⁵

A control valve for small flow rates³⁶ of less than 0.1 gal/min with a maximum outlet pressure of 30,000 psi is shown in Fig. 5-23b. The valve

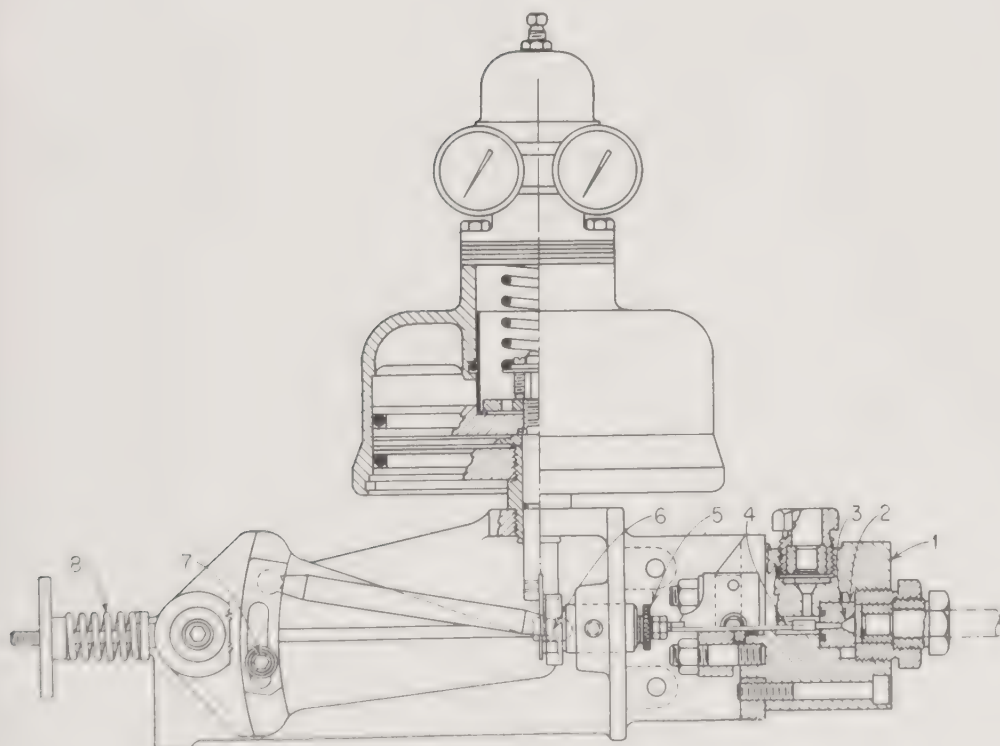
³⁴ F. A. Ernst and F. C. Reed, *Chem. & Met. Eng.*, **37**:580 (1930).

³⁵ A. T. Larson and S. Karrer, *Ind. Eng. Chem.*, **14**:1012 (1922).

³⁶ The Annin Company, Bulletin 50 WW.



(a)



(b)

FIG. 5-23. (a) Back-pressure regulator. [From A. M. Whitehouse, P. L. Golden, R. W. Hiteshue, and E. L. Clark, *Chem. Eng. Progr.*, **49**:491 (1953).] (b) Control valve. (The Annin Company, Los Angeles, Calif.) 1. Valve body. 2. Valve seat. 3. Inlet. 4. Valve stem with stellite plug. 5. Thumb set. 6. Crosshead and drive rod. 7. Stroke adjustment. 8. Loading spring.

has a removable stellite seat (2) and a hard chromium-plated highly polished valve stem (4) with a stellite plug, which fits the seat. The stem is packed with a combination teflon O ring and V ring. The stem is operated by a cross-head and drive-rod assembly (6), and the stroke and the valve action are adjustable (7).

Rupture Safety Disk. The rupture disk provides a means of rapidly relieving excess gas pressure. The pressure at which the disk will rupture depends upon the material and thickness of the disk as well as

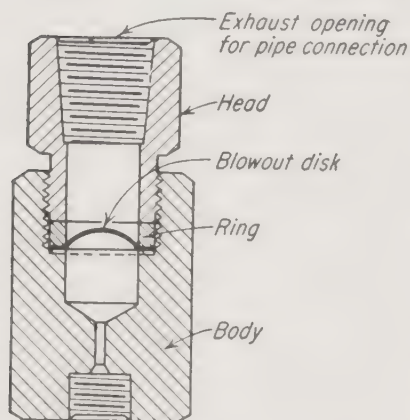


FIG. 5-24. Rupture-disk assembly. (American Instrument Company, Inc.)

upon the design of the clamping arrangement for holding it. A rupture-disk assembly is shown in cross section in Fig. 5-24. In this design the downstream side of the rupture disk is provided with standard pipe threads for connecting to an exhaust pipe. When flammable or poison gases are being handled, it is important to avoid discharging these gases to a region in which a secondary explosion may take place or a toxic hazard may be set up. An investigation of the design and application of rupture disks is described by Prescott.³⁷

5-4. Electric Connections. Electric

heating elements, thermocouples, and liquid-level contacting points within a high-pressure vessel require the introduction of electric leads through the walls. These must be insulated from electric contact with the wall. Several methods of doing this are shown in Fig. 5-25a to e. One similar to that in Fig. 5-25a has been described by Bone³⁸ and was originally used by Amagat. It is useful at relatively low temperatures or where the insulating pressure seal is not subjected to high temperature. The design at the right consists of an electric conductor with a suitable cone on the end toward the pressure side of the vessel wall. A plastic hollow cone fits over the conductor and provides the pressure seal against a like cone turned in the wall of the plug which enters the pressure vessel. The inner end of the conductor is heated to soften the plastic, and the plug on the top of the insulating washer is tightened. This procedure may be repeated several times, and the inner end of the seal may be finished by applying zinc oxychloride cement. The cone on the conductor prevents it from

³⁷ G. R. Prescott, *Trans. ASME*, **75**:355 (1953).

³⁸ W. A. Bone, D. M. Newitt, and D. A. T. Townend, "Gaseous Combustion at High Pressures," Longmans, Green & Co., Ltd., London, 1929.

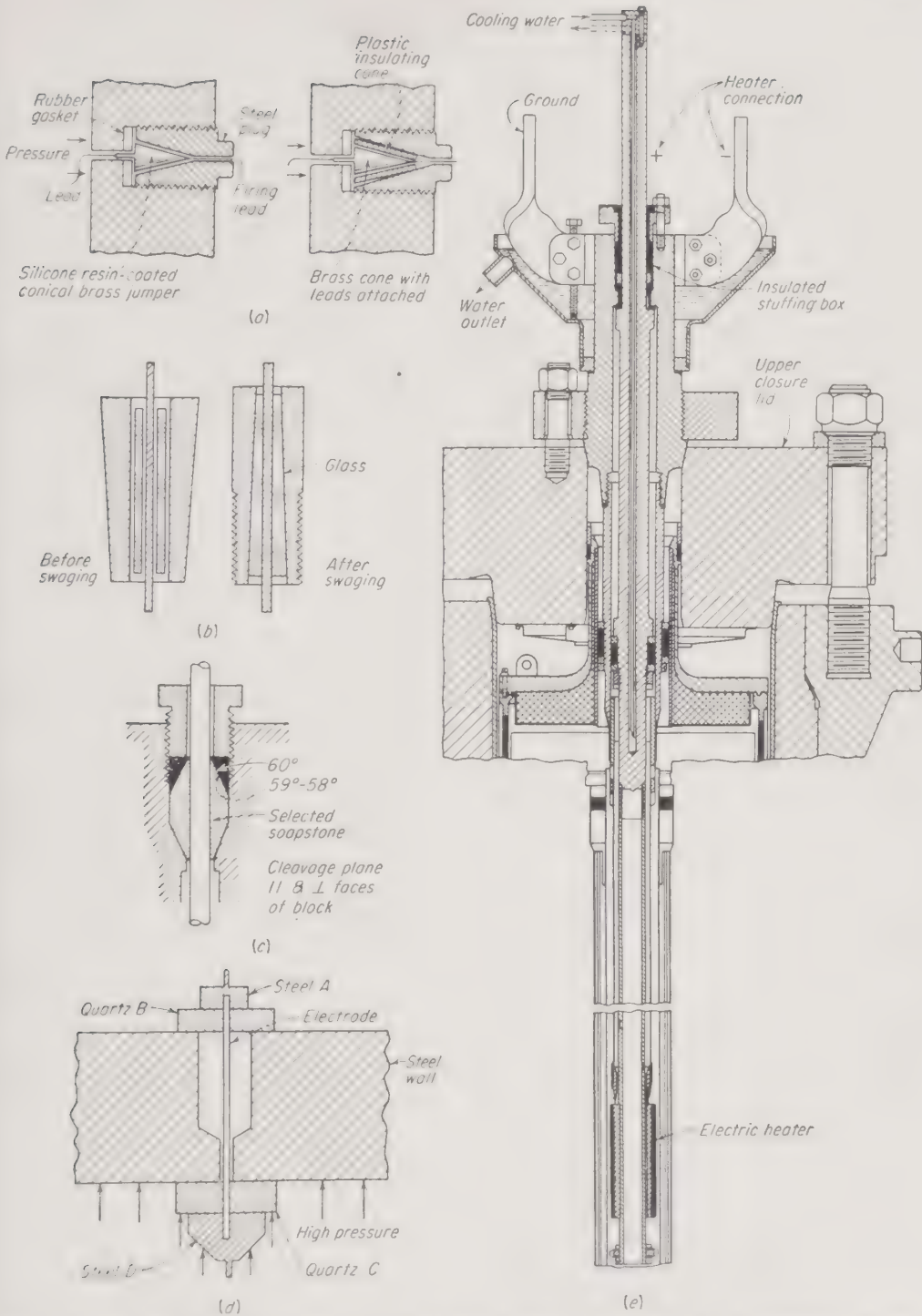


FIG. 5-25. Electric connections. (a) Brass cone. [From E. J. Mickewicz, *Trans. ASME*, **75**:325 (1953).] (b) General Electric Company glass seal. (c) Double-cone soapstone seal. (d) Electric connection. [From A. Michels and C. Michels, *Trans. Roy. Soc. (London)*, **231A**:409 (1953).] (e) Industrial connection. (Adapted from U.S. Off. of the Pub. Bd. Rept. 52193.)

being blown out even though the plastic cone should fail. Mickewicz³⁹ reports improved performance when the plastic cone is replaced by a silicone resin coating on the brass cone as shown at the left. Another type of electric inlet is shown in Fig. 5-25*b* and is useful for pressures of 300 atm and at temperatures as high as 450°C. The connection is manufactured by General Electric Company according to the patent by Mackay.⁴⁰ When two or more leads are to pass through the same fitting, a hole is drilled through the plug and reamed to a conical shape with the larger diameter at the high-pressure side. The conduit is encased in a glass sheath, and the latter is pressed in place at a temperature at which the glass is plastic. When only one lead is to be passed through a cylindrical plug, the latter is drilled with a hole of uniform diameter and turned to a conical shape on the outside. The electric conductor, glass sheath, and plugs are then assembled, heated, and swaged until the shell is conical on the inside and cylindrical on the outside, with the glass filling the inner cone. Cracks appearing in the glass may be filled with waterglass. The conical shape prevents the glass plug and conductor from being blown out by the internal pressure.

The seal shown in Fig. 5-25*c* has been used by the Fixed Nitrogen Research Laboratory for both high pressures and high temperatures. In this design, the insulating pressure seal is made by a double-cone soapstone insert. A steel pressure ring with a cone cut in the lower surface matches the upper cone of the soapstone. The cones on the soapstone (58 to 59°) and steel (60°) are cut at slightly different angles to provide essentially line contact. The soapstone must be deformed sufficiently to provide a seal around the surface of the conductor, and the shear planes in the soapstone are best orientated parallel or normal to the plug faces to permit this deformation. A plastic such as polystyrene is suitable for low temperatures. Insulating plastic tubes may be used around the conductor on both sides of the cone. A shoulder may be added on the conductor on the pressure side to prevent it from being blown out in case of failure of the seal. Within the pressure limits for which it has been designed, an ordinary automobile spark plug provides an excellent high-pressure lead.

An electric connection described by Michels is shown in Fig. 5-25*d*. The vessel steel wall is shown. The electrode passes through the wall and is insulated from electric contact with it by the quartz disks *B* and *C*. The electrode screws into the steel plugs *A* and *D*. The upper surface of the steel plug *D*, the lower surface of the steel wall and both surfaces of the quartz disk *C* are ground optically flat. The steel plug *A* is screwed up tight to provide an initial seal. The steel wall and the

³⁹ E. J. Mickewicz, *Trans. ASME*, **75**:325 (1953).

⁴⁰ G. M. J. Mackay, U.S. patent 1,456,110 (1923).

parts *C* and *D* may be held together by a thin layer of adhesive, but the closure is formed by the internal pressure. Bridgman has another design.¹²

Electric conductors for relatively heavy duty, such as the leads to the heating elements in synthetic-ammonia converters, require special attention. In a typical connection designed for this purpose and described by Hunter,⁴¹ the high-pressure-vessel wall serves as one lead while the other is in the form of a tube passing through the head. This tube is equipped with water-cooling and is of sufficient length so that the electric-insulating pressure seal is removed from the high-temperature part of the converter. The conductor tube is centered in place by insulating rings at several points along its length. An industrial electrode is shown in Fig. 5-25*e*.

5-5. Windows and Sight Glasses. To observe a liquid level or note the appearance of a liquid or gas, it is convenient to use a high-pressure sight glass. Windows are used to transmit light in various applications. The design of a sight glass is illustrated in Fig. 5-26*a*. These are limited not so much by the maximum compressive stress to which the glass may be subjected, as by the inability of the glass to distribute a localized stress over a large area. If a high stress concentration results from tightening bolts, from unequal thermal expansion between the glass and metal, or from slight misalignment of the glass-metal surfaces, the glass is likely to crack and fail at these points. In the design shown, the glass is free to move in a lateral direction and the sealing pressure on its surfaces is applied by relatively soft gasket material, which also allows movement. The concentrated force applied by the bolts does not act directly on the glass.)

In a typical design.

If it is necessary to observe only a liquid level, this can be accomplished with a single glass of the reflex-gauge type. This gauge does not require illumination from the back, as vertical grooves cut in the inside surface cause the liquid to appear black with a sharp line at the interface between gas and liquid, contrasting with a bright mirrorlike appearance in the gas space. The Diamond Power Specialty Company supplies a Multi-port gauge with an optical system so that water shows green and steam shows red.

A very simple design of window has been described by Poulter^{42,43} for pressures as high as 30,000 atm. Bridgman has used this design at pressures of several thousand atmospheres, and a modification of these designs is shown in Fig. 5-26*b*. A hole is provided in a plug, and a flat glass surface is placed over this hole and fastened with adhesive to keep it in place. The high pressure acting on the inner surface of the glass is

⁴¹ R. M. Hunter, *OPB Rept.* 129, June 2, 1945.

⁴² T. C. Poulter, *Phys. Rev.*, **35**:297 (1930).

⁴³ J. R. Collins, *Phys. Rev.*, **36**:305 (1930).

sufficient to provide a good seal at the glass-metal surface. Since the glass is not confined in any direction, it is free to move and relieve localized stresses. The glass surfaces which make contact must be flat and carefully finished but need not be of optical flatness.

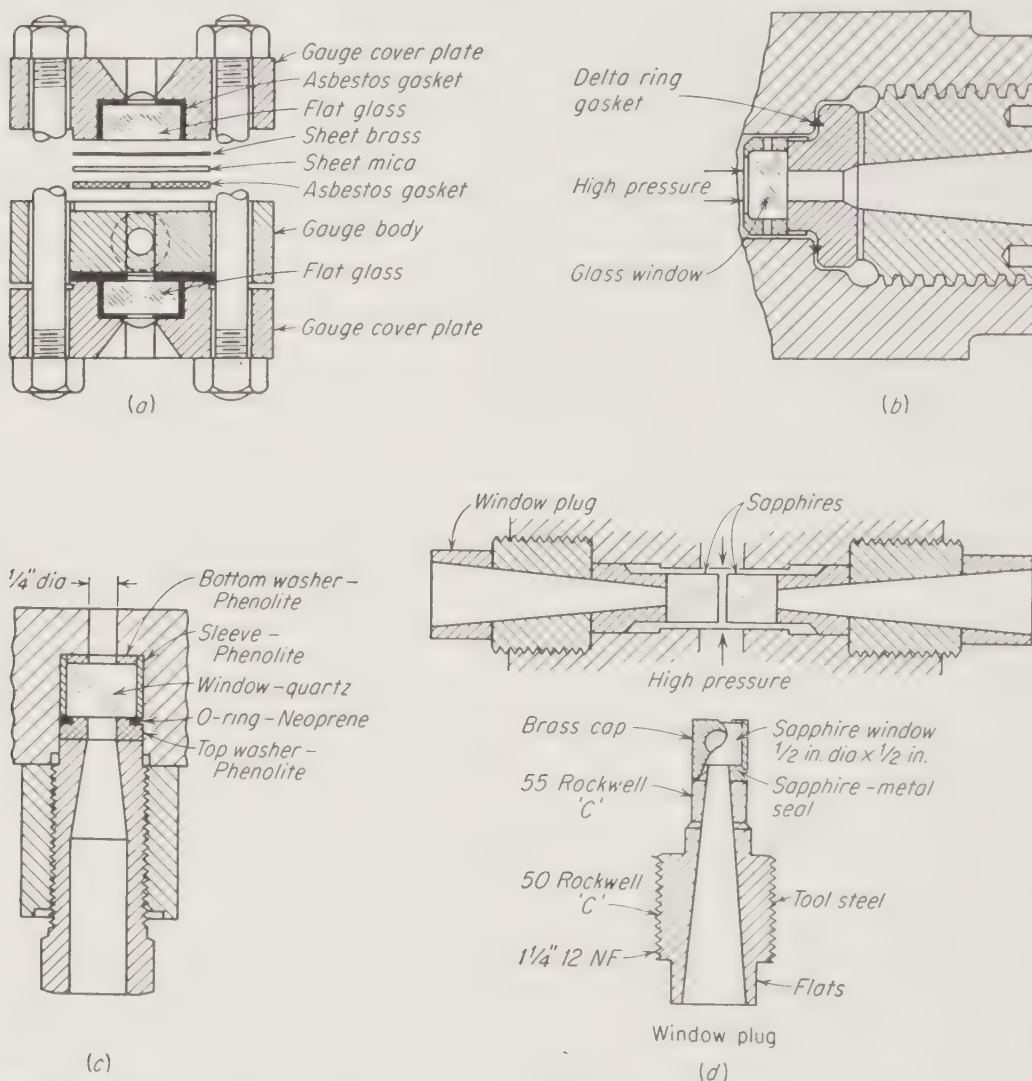


FIG. 5-26. Windows and sight glasses. (a) Sight glass. (Diamond Power Specialty Company.) (b) Glass window. (From T. C. Poulter,⁴² J. R. Collins,⁴³ and P. W. Bridgman, American Instrument Company.) (c) O-ring closure for quartz window. (Autoclave Engineers Inc.) (d) Sapphire window for 12,000 atm. (From E. Fishman and H. G. Drickamer, *Ind. Eng. Chem.*)

Another modification, which uses an O ring to seal the window, is shown in Fig. 5-26c. At higher pressures, care must be used in selecting the hardness of the steel plug which supports the window. Drickamer⁴⁴

⁴⁴ H. G. Drickamer, K. D. Timmerhaus, and L. H. Tung, *Chem. Eng. Progr.*, **49**:503 (1953); E. Fishman and H. G. Drickamer, *Ind. Eng. Chem.* (to be published).

describes a sapphire window using the Poulter principle for making spectroscopic and light-scattering observations at pressures up to 12,000 atm.

This window is shown in Fig. 5-26*d*. The plug is made from Columbia Superdie Tool steel. In order to make the plug surface hard enough to seat the window without deforming and yet tough enough to avoid cracks in the threads, the seating face is made with a hardness of 55 to 56 Rockwell C and the threads with about 50 Rockwell C. The face of the plug is surface-ground and lapped on 0000 emery paper. Curvature of the surface may be prevented by screwing the plug into a 1½- to 2-in.-diameter lapping block. The sapphire-metal seal is satisfactory when

TABLE 5-1. BURSTING TEST ON GLASS TUBES†

OD, mm	ID, mm	Ratio of diameters	Bursting pressure, atm
5.8	0.46	12.60	1,200
6.7	0.24	27.90	1,100
9.2	3.00	3.06	380
10.4	4.00	2.60	240
3.8	2.42	1.57	283
6.4	4.78	1.34	221

† From W. A. Bone, D. M. Newitt, and D. A. T. Townend, "Gaseous Combustion at High Pressures," Longmans, Green & Co., Ltd., London, 1929.

the window cannot be blown off orally from underneath, or when the plug can be picked up by lifting the window. Linde synthetic sapphires are convenient. The *C* axis of the crystal must be perpendicular to the window face. A flatness of at least 0.0001 in. may be specified when purchasing, and this is almost always satisfactory. Otherwise the window must be lapped with diamond paste.

Windows of quartz or glass in the form of a cone have been used in designs similar to that described for electric leads in Fig. 5-25*b*. While these have been used successfully at pressures up to 400 atm, the glass is subjected to relatively high radial compressive stresses which ultimately cause the windows to crack. Ordinary cylindrical sight glasses, as commonly used at lower pressures, would also be satisfactory at higher pressures if only the bursting strength of the glass need be considered. However, most attempts at designing a suitable gauge glass of this sort have been unsuccessful in distributing the stresses localized at the pressure seal, and these glasses have been unsatisfactory in most cases.

The results of bursting tests on glass tubes described by Onnes and Braak are shown in Table 5-1. Such tests are not very reproducible, and the results should be used with care.

5-6. Moving Shafts. The design of valves, pumps, gas compressors, and agitators for reaction vessels requires that a moving shaft be sealed against a high internal pressure. The shaft either rotates or moves back and forth in the direction of its axis. The seal is usually formed in a relatively long chamber which surrounds the shaft and is called a stuffing box.

Several types of packing for such service are shown in Fig. 5-27*a* to *e*. A type of packing developed by the Fixed Nitrogen Research Laboratory is shown in Fig. 5-27*a* and consists of a series of rings of bearing metal in the shape of an X separated by steel rings with a diamond-shaped cross section. As pressure is applied to the end of the stuffing box, the steel rings serve to press the bars of the X against the shaft to maintain a close fit. Another type of packing, the S.E.A. ring, or Seatrist Gland Ring, was developed in England and is shown in Fig. 5-27*b*. These rings are made of softer material, such as a rubber-and-graphite composition, on a reinforcing web of cotton or asbestos and are provided with a slot forming a thin edge next to the moving shaft. The higher pressure should be at the open end of these slots with a pressure gradient across each ring of packing. This gradient serves to press the thin edge of the ring against the piston to form a seal. The design is most suited to sealing in the case of pressure from one side only, and, when used on double-acting pistons, two sets of rings are required with the slot openings facing in opposite directions in each set. A third type is used when the piston acts against a liquid as in a hydraulic pump or when the shaft is turned slowly and at rather infrequent intervals as in a valve stem. The problem of packing is then not so severe. A typical arrangement for this service is shown in Fig. 5-27*c*. Other types of packing are shown in Fig. 5-27*d* and *e*.

An ingenious seal suggested by J. L. M. Morrison^{44a} is shown in Fig. 5-27*f*. This prevents leakage along a shaft with a negligible frictional restraint for rotation or movement in the axial direction. The seal consists of a relatively large "body" of metal subjected to pressure on all sides with a lip extending along the shaft on the low-pressure side. Leakage around the outside of the body is prevented by an unsupported area packing. Since the body is subjected to uniform fluid pressure in all directions, it will not change dimensions and will restrain the high-pressure end of the lip from moving radially. However, the lip is subjected on its external diameter to a pressure greater than the fluid pressure in the vessel over the width of the rubber packing and on its internal diameter to a pressure varying from the fluid to atmospheric pressure along the length of the seal. With a proper choice of dimensions, the clearance between the shaft and the seal will not change appreciably with pressure as the forces acting on the lip will be balanced. For a small leakage, the

^{44a} B. Crossland, *Proc. Inst. Mech. Engrs. (London)*, **168**:935 (1954).

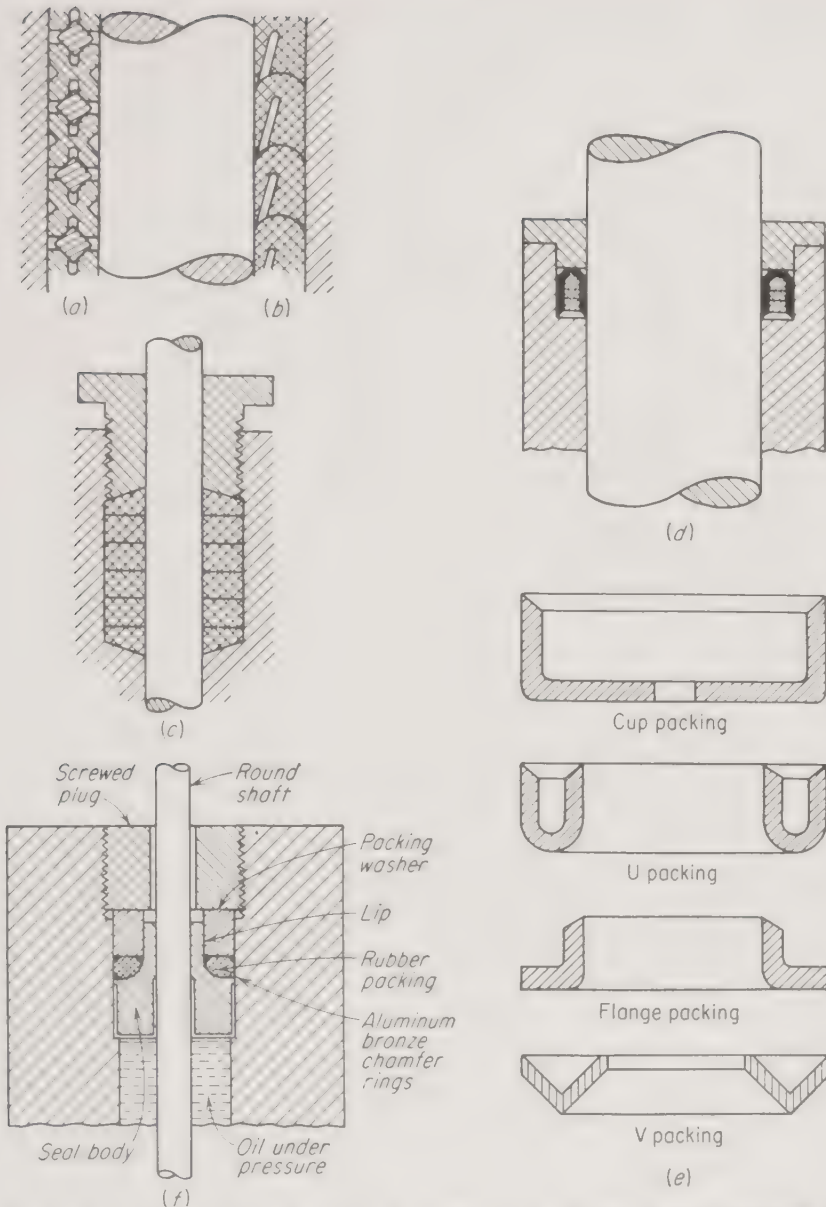


FIG. 5-27. Packing for sealing a moving shaft. (a) (From *Fixed Nitrogen Research Laboratory*.) (b) SEA rings or Seatrist gland rings. (From *Ronald Trist and Company, Ltd., and Johns Manville Corporation*.) (c) Valve-stem packing. (d) U leather packing on a pump plunger. (Graton & Knight Company.) (e) Leather packing rings. (Graton & Knight Company.) (f) The Morrison seal. [*B. Crossland, Proc. Inst. Mech. Engrs. (London)*, **168**:935 (1954).]

clearance between the shaft and seal must be small. By external and internal honing, a clearance of 0.00005 in. or less has been obtained.

The seal for a rotating shaft is not needed if the driving motor is enclosed inside the high-pressure vessel. The "canned" motor represents such a design. Pressure Products Industries and Chem-pump Corporation

have adapted this design for driving an agitator at speeds of 600 rpm and higher, in vessels of relatively large capacity, under pressures up to 10,000 psi. For smaller vessels up to 50 gal, the magnetic, or solenoid, type of agitator, patented by the Standard Oil Company (Indiana) and called the Magne-Dash, is used.

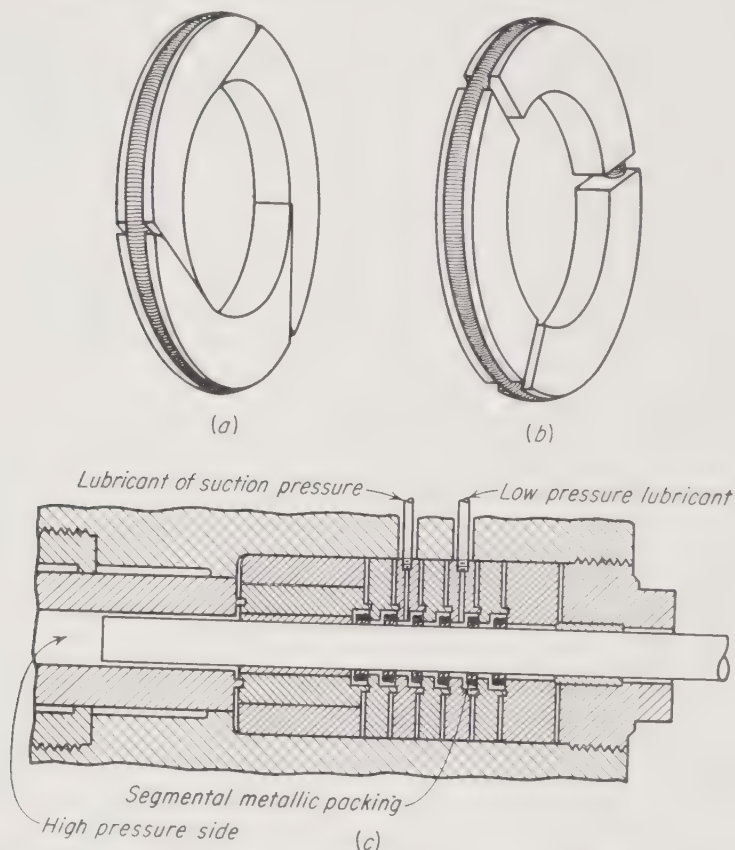


FIG. 5-28. Metal packing. [From Walter Coopey, *Chem. Eng.*, **58**(7):116 and **58**(11):164 (1951).] (a) Metal packing ring segmented tangentially. (b) Ring with radial cut. (c) Packing case for metal rings.

Metal piston rings are used in packing piston rods for high-pressure gas compressors. These are comparable to the piston rings used on automobile pistons but are of somewhat more complicated construction. Metal-ring packing⁴⁵ is shown in Fig. 5-28a and b. The ring in Fig. 5-28a is cut in three segments such that the cuts lie along the three sides of an equilateral triangle with the sides of the triangle parallel to, but displaced outward from, a tangent to the inner circle. As wear takes place on the inner circle, the three segments move simultaneously an equal distance toward the center and thus compensate for the wear. In the ring in Fig. 5-28b the segments are cut radially. These rings are used in pairs, each pair fitting in a separate groove or cup with several cups

⁴⁵ Walter Coopey, *Chem. Eng.*, **58**(7):116 (1951); *ibid.*, (11):164 (1951).

combined to make up a packing case, as shown in Fig. 5-28c. The packing case is sealed on the inside by a ring gasket. Lubricating oil is fed to the top of the shaft at one or two points between the pairs of packing rings. Provision is also made between two cups to drain off condensate or to vent gases which leak through the rings. Other packing rings designed on a similar principle have been developed. These metal rings depend on maintaining a small clearance between the inner diameter of the ring and the outer diameter of the moving shaft. Slots and grooves in the ring are sealed in the axial direction either by an adjacent ring or by the walls of the cup in which the rings fit. Thus the sides of a pair of rings are carefully ground and lapped to close tolerances. A garter spring in a groove around the outer diameter of the ring holds the segments together during assembly and before pressure is applied. Sommers⁴⁶ points out that the pressure of the ring against the moving shaft is provided principally by the fluid pressure acting radially against the outer diameter of the ring. A packing ring with an outer circumferential area of 4.18 sq in. and an inner area of 2.95 sq in., if used to seal a pressure of 2,000 psi, would exert a bearing pressure on the moving shaft of from 2,840 to 835 psi depending upon whether or not one assumes that the pressure also acts on the inner diameter of the packing ring. Such a pressure is likely to be excessive, and it may be important to keep the outer diameter of the metal ring to a minimum. This can be done by building the ring in a set of two or three concentric layers. The rings themselves may be made of cast iron, bronze, Bakelite or carbon Bakelite, and similar material. They have been used to pack compressors successfully at pressures up to 30,000 psi. The rate of oil fed is of considerable importance, and excessively high rates are damaging as well as low rates which produce insufficient lubrication. When too much oil is supplied, it raises the pressure acting on the outer diameter of the packing ring to a greater extent than is necessary and thus increases ring wear and may lead to scoring and gas leakage.

The principles of packing reciprocating rods and rotating shafts operating at high pressures and at relatively high speeds are stated by Coopey.⁴⁵ Seals for *rotating shafts* will be considered first. Soft or plastic packing in a conventional stuffing box is a constant source of trouble. No matter how carefully the packing is installed and adjusted, a scored shaft usually develops, resulting in a leaky seal.

Rotating Shafts. There are two approaches to designing a satisfactory high-pressure seal for a rotating shaft. The construction may be rigid with very close clearances between the shaft and packing, or these elements may be flexible and designed to compensate for the difficulties which cannot be eliminated. The first approach is satisfactory in a

⁴⁶ H. A. Sommers, *Chem. & Met. Eng.*, **37**:574 (1930).

limited number of small-scale or laboratory units, but serious difficulties are encountered in larger-scale units. These arise because of misalignment, distortion due to pressure and temperature, and the poor lubricating properties of the process fluids. The problems to be encountered are indicated by the following list:⁴⁵

1. Precision workmanship within tens of thousandths of an inch is necessary to obtain the required clearances.
2. Running clearances will be different after the pressure of the lubricant and the process have been applied.
3. If the process is operated at elevated temperatures, conduction of heat will introduce expansion problems in the stuffing box.
4. Shearing action in the oil film develops heat which may have to be removed by a cooling medium. Otherwise it may give rise to the temperature effect just mentioned or may reduce the viscosity of the lubricant to such an extent that it will not seal satisfactorily.
5. Selection of the proper lubricant must be based not only on its viscosity under operating conditions but also on its possible effect on the process. Since an appreciable quantity of the lubricant will pass into the pressure vessel being sealed, it must not be a contaminant for the reaction.
6. Because of the variables involved, it is impossible to calculate with any degree of accuracy the conditions under which the seal will operate.

Two rotary seals . . . designed to overcome . . . these difficulties [are shown]. They both involve the introduction of lubricant at process pressure between a pair of sealing elements. This can be done in two ways [Fig. 5-29a]. The solid line diagram shows a lubricant reservoir connected to the seal at two points. Process pressure from the lower tap is imposed on the lubricant in the reservoir, forcing it into the upper tap at this pressure. The lower element is thus at balanced pressure, and there will be no flow of fluid across it in either direction. The upper element [Fig. 5-29a] . . . is subjected to full process pressure.

In the broken line arrangement, a high pressure lubricator forces lubricant between the packing elements. A high pressure reservoir catches the lubricant in excess of that necessary to maintain balanced pressure. Modifications of these schemes can be used but, in general, the solid line arrangement is more suitable for use with the type of seal shown in [Fig. 5-29b] and the alternate method with that of [Fig. 5-29c].

The . . . details of the seals are shown [in Fig. 5-29b and c]. Both use a metal packing element for the lower seal. This element may be made of silver, bronze, or any other metal or alloy which has suitable anti-friction properties. Because of the negligible pressure differential across the element, . . . a plastic material [may be used]. The only difference between the two designs as far as the lower element is concerned is that [Fig. 5-29b] shows an O-ring and [Fig. 5-29c] shows a Belleville cone-shaped spring and squeeze ring combination. Although the Belleville spring has the advantage of compactness, a helical spring or any other type that will produce the same results can be used.

In either case, their purpose is to maintain lip contact of the packing element

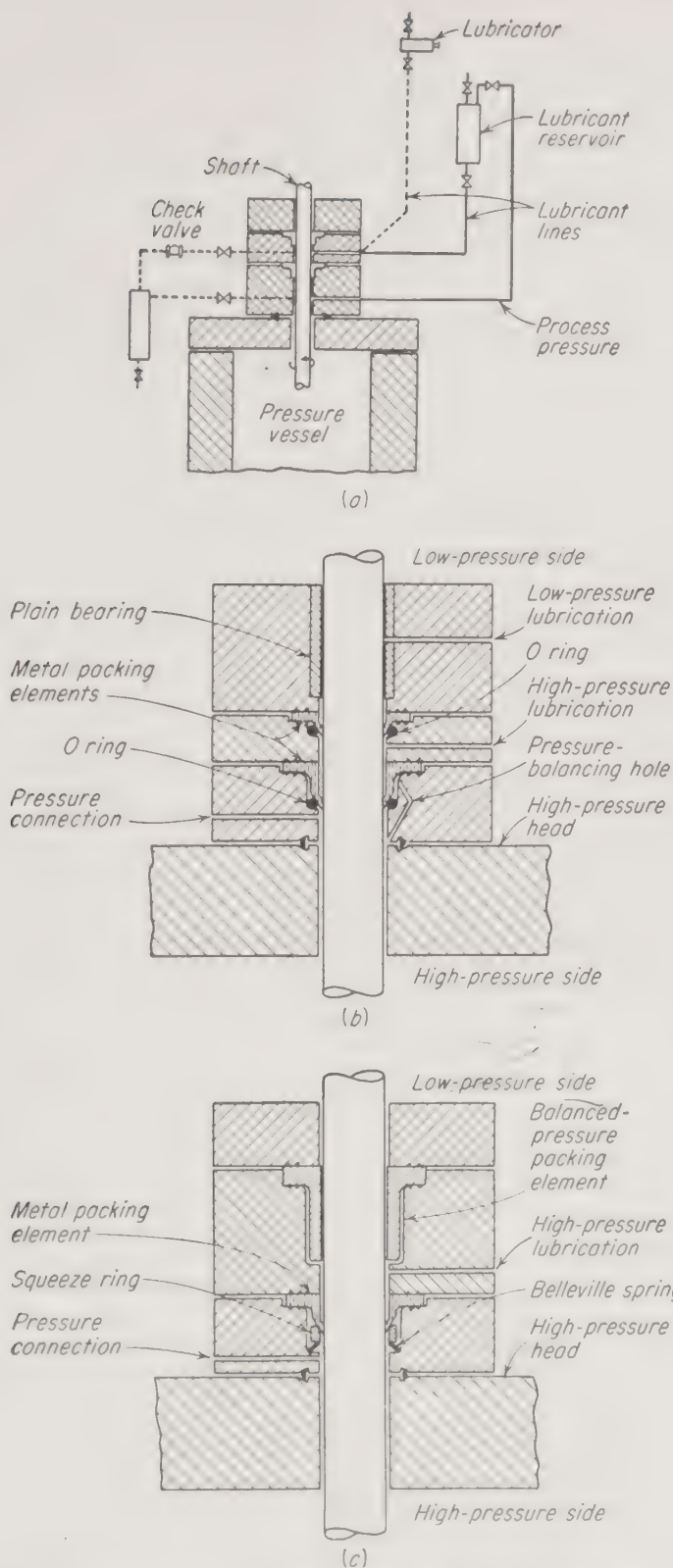


FIG. 5-29. Seals for rotating shafts. [From Waller Coopey, *Chem. Eng.*, 58(7):116 and 58(11):164 (1951).] (a) Lubricating systems. (b) O-ring seal. (c) Spring seal.

with the shaft. If the lip of the packing is formed to provide only line contact, wear will be negligible. A hole in the lower packing retainer in [Fig. 5-29b] or a small hole through the spring in [Fig. 5-29c] permits pressure equalization across the lower element. In [Fig. 5-29c] a small groove across the spring seat would serve the same purpose. As a result of this balanced pressure across the lower element, it is necessary to retain only the lubricant pressure, which is relatively easy. The two designs of lower seal elements are based on the same principle and differ only in the method used to maintain contact of the packing with the shaft. They can be used interchangeably.

The upper element of [Fig. 5-29b] is designed on the Bridgman "unsupported area" principle. . . . The O-ring in the upper element provides the initial lip contact of the packing with the shaft. After pressure is developed by the lubricant, contact is retained by the unsupported area or unbalanced pressure effect. Clearance above the O-ring must be at a minimum, or else the ring material will be forced into it and lose some of its effectiveness. The ring, because of its resilient nature, transmits the pressure to the packing element.

With a close initial fit of the packing on the shaft, the O-ring would be unnecessary. Its use provides compensation for any wear that may take place. Such wear should occur very slowly, since the rubbing surfaces are well lubricated. After interruptions in operation, however, it would be difficult, without some such means of adjustment, to build up sufficient pressure with the small flow of lubricant available to effect sealing between the lip of the packing and the shaft.

The material of which the O-ring is made determines the maximum temperature at which the packing can be operated. The temperature effect can, however, be minimized by increasing the distance between the pressure vessel and the packing or by using some method of cooling.

The plain bearing shown above the packing provides alignment in the assembly. It is lubricated from a low-pressure source. If only one set of packing is used, a thrust bearing is required. It would have to be large enough to take the total pressure load over the cross-section of the shaft. If the shaft extends through both ends of the vessel and is packed at each end, then there is no need for a thrust bearing.

The upper packing element of [Fig. 5-29c] is a balanced pressure sleeve or bushing which acts both as a packing and a bearing. The clearance around the outside of the bushing allows the same pressure to exist on both sides of the wall of the bushing. This means that the clearance between the bushing and the shaft will remain essentially constant in spite of variations in pressure.

The clearance should be made a close running fit so that the pressure drop of the lubricant film across the length of the bushing balances the operating pressure. The amount of lubricant leakage will depend upon the clearance that is used and the operating pressure maintained.

Advantages of these seals are simplicity, low cost, wide choice in lubricants, protection of the process against contamination, and minimum lubricant consumption.

Methods for packing rods which are rotated slowly and infrequently are illustrated in Sec. 5-3.

Reciprocating Shafts. Problems are also encountered with reciprocating rods. No formulas exist as yet for the satisfactory design of packing glands for this case, and, according to Coopey, the design must be based largely on know-how and experience. Important factors are the alignment of the rod in the bearing, the rod lubrication, the choice of material for the rod, the packing, the packing lubrication, and the surface finish on the materials. The packing should never be used to support or align the rod. Its sole function is to hold the fluid pressure with a minimum of frictional resistance.

Rods may be made from steel that can be heat-treated, carburized, nitrided, or chromium-plated. Heat-treated steels may be satisfactory with a scleroscope hardness of 50; surface-hardened material should be 80 or higher. Corrosive conditions suggest a stainless steel that can be hardened or possibly a special design of the stuffing box. The packing may be of the soft or metallic types. The concept of the requirements of a packing is not well understood, and there are no distinctly defined applications; but soft or plastic packings are usually selected for liquids and metallic packings for gases.

The soft packing category includes a wide variety of materials, such as cotton, asbestos, hemp, flax, rubber and plastics, which may be combined with some of the soft metals in shredded foil form. The most desirable form is a ring which has been properly shaped and compressed to the stuffing box dimensions. Although the chevron and V shapes are supposed to be self-sealing, they actually are not. The advantage of these packings is that they are made of a tough, fibrous material which has a fair amount of resiliency. After a short period of high-pressure operation all soft packings are formed into a compact mass that has lost any self-sealing characteristic it may have had originally.⁴⁵

The proper design of the rod and stuffing box will do away with the old practice of breaking in or wearing in. The breaking-in process cannot be controlled and frequently results in nonuniform wear of rod and packing. With a soft packing, a small amount of running in may be necessary to seat and compress the packing, but the time required for this is greatly reduced by precompression. By starting with highly finished and fitted surfaces, the breaking in can be entirely eliminated.

No packing, regardless of type, can be expected to operate satisfactorily for any length of time without proper and dependable lubrication. Three types of *lubrication* are generally recognized—hydrodynamic, boundary, and thin-film. With hydrodynamic lubrication the surfaces are definitely separated by a film of fluid whose physical properties are not affected by the thickness of the film. With boundary lubrication there is actual contact of the moving surfaces. This means that the chemical and physical-chemical properties of the lubricant are of utmost importance, and the bulk physical properties, . . . are of little consequence. Friction in hydrodynamic lubrication depends upon the viscosity of the

lubricant, but with a packing where boundary conditions exist and the film thickness is too small to establish hydrodynamic conditions, the importance of viscosity diminishes.

Because thin-film lubrication is intermediate between the other two types, it may be assumed that the bulk physical, the chemical and the physical-chemical properties of the lubricant are all important. Thin-film lubrication is a fairly new concept and further information on the phenomena involved is needed. If conditions permit, it is desirable where thin-film lubrication seems to exist to use a lubricant which combines the desirable properties for both hydrodynamic and boundary lubrication.

There may be definite limitations, because of process considerations, on the kind of lubricant that can be used. This may require that the packing and stuffing box be designed accordingly. Another important factor is the material of construction used for the packing. If the service is corrosive, a corrosion-resistant ductile metal may be required, which would mean boundary lubrication between metals. The . . . allowable minimum thickness of an oil film is mainly dependent upon the mechanical finish of the surfaces. If the surfaces are polished, they will . . . be capable of operating with thinner oil films.

The main properties of lubricants are viscosity and oiliness, but they must be evaluated for the conditions of service. Viscosity changes with temperature and pressure, but viscosity may mean little if the lubricant is soluble in the process fluid. A relatively poor lubricant in the generally accepted sense may, under some conditions, be much better than one which would otherwise be considered an excellent lubricant.

There is a wide field to select from in the mineral, compounded, vegetable and animal oils, and in the large number of newly developed synthetic lubricants. Even one of the reactants might be acceptable. Any effort to find a fluid that is satisfactory from a chemical standpoint and also has adequate lubricating properties is justified. It will help forestall trouble. . . .

It is essential that all parts be made to dimensions; that they be absolutely free from dirt and grit; that there be no feather edges to break off and cause trouble; that the lubricating system function and deliver before operation is started; and that any abnormal condition be remedied instead of trying to apply a palliative. While these points may seem obvious, they are frequently overlooked.⁴⁵

The application of these principles is illustrated by a few packing installations.

In [Fig. 5-30a] is shown the most simple type of soft or plastic packing installation. Proper alignment is provided for by a floating connection between the piston and the crosshead. This arrangement is intended to compensate for a radial out-of-alignment of only a few thousandths of an inch. The end of the piston is flat, although there has been a tendency by some designers to make a ball joint connection. The latter might provide for angular misalignment but there should not be any.

The lubricant is introduced at the outer or low-pressure end of the packing. This method is recommended for all packing installations. While it has been

common practice to introduce lubricant at the high-pressure end of the packing on the basis that it will work out through the packing, this design is not based upon sound reasoning. Here is what is wrong with it:

1. It depends upon a slight leakage, but if a leak starts at high pressure, it quickly becomes worse.

2. Although the packing at the outer end of the stuffing box is the most highly compressed and receives the most wear, it gets the poorest lubrication.

3. An oil hole through the cylinder wall in the high-pressure zone is a point of high stress concentration which will cause fatigue failure.

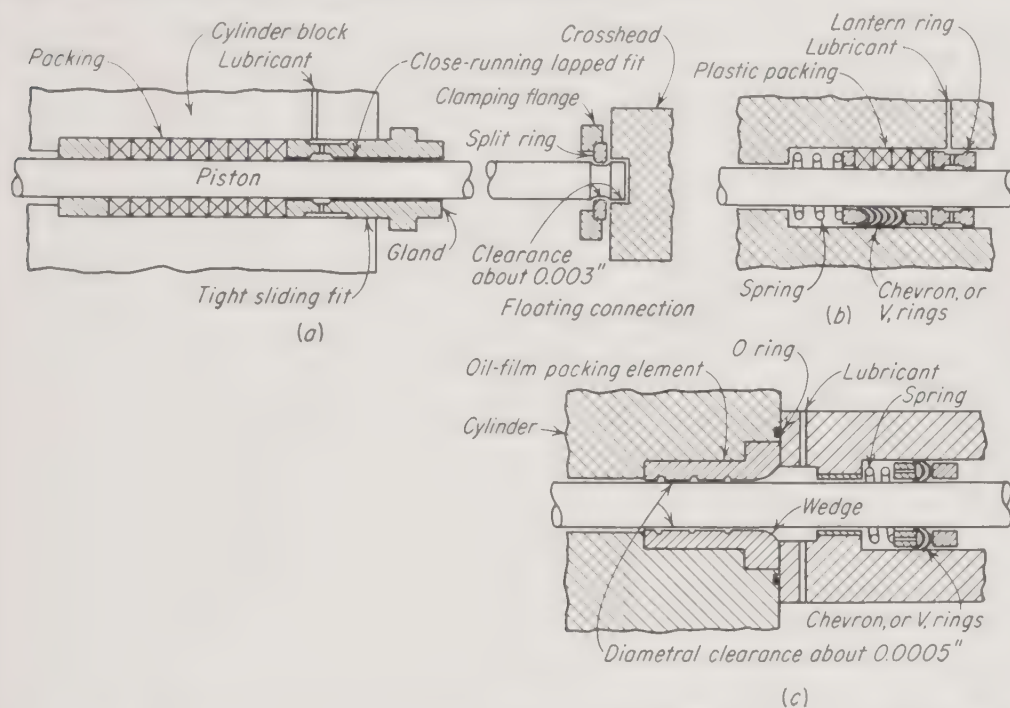


FIG. 5-30. Packing for reciprocating shafts. [From Walter Coopey, *Chem. Eng.*, 58(7):116 and 58(11):164 (1951).] (a) Soft-packing installation. (b) Spring-loaded packing rings. (c) Wedge action.

4. Adding the lubricant to the process fluid causes a deterioration in lubricating properties.

5. If the lubricant is a contaminant, it is put where it hurts the most.

6. The lubricating system must be designed for the maximum pressure.

With the recommended system, . . . a pressure only slightly higher than the pump suction pressure [is needed]. The lubricant is forced through the length of the packing, and even at the highest pressures for which this packing can be used it will be found that some lubricant has entered the cylinder. The packing which receives the most severe service is sure to be well lubricated.

The packing arrangement in [Fig. 5-30b] is similar to that in [Fig. 5-30a] with two exceptions. The lower half of the sketch shows a stack of chevron or V packing rings, and at the high-pressure end of the stuffing box, with either type of packing, [there] is a large helical spring. The spring is [very] important. With soft or plastic packing a void occurs at the bottom of the packing after a

period of service, owing to compression and wear. This void permits the lower rings to float around somewhat loosely. If adjustment of the gland is delayed too long, leakage occurs. The purpose of the spring, therefore, is to keep a light load on the bottom of the packing, particularly on the suction stroke. On the discharge stroke the fluid pressure compresses the packing so that leakage is prevented until it is caused by wear. The action tends to be automatic. Lubricant is supplied at a pressure above suction so it is forced between the packing and the piston on the suction stroke. It is a case of boundary lubrication, with the film being renewed on each stroke.

Metallic packings of the segmental type are best adapted for gas compression. [Fig. 5-28c] shows an application which is conventional except for the way in which the lubricant is supplied—between each two sets of rings—and the number of rings. Excessive packing of any kind can do more harm than good unless each ring receives an adequate supply of lubricant. Six rings should be sufficient for any pressure up to 20,000 psi.

Although it is considered that the rings “float,” they will not do this at high pressures. If the suction pressure is low, there can be some movement on the suction stroke, but in the higher stages of a multi-stage compressor or in a high-pressure recycling compressor there will be no floating. Because of this, the preparation of the packing and the application of the lubricant need special attention.

Under some conditions an approach to thin-film lubrication may exist, but as a rule it is of the boundary type. This requires careful selection of the metal for the packing rings so that they will have some anti-friction properties. Generally the bronzes are a first choice although, when conditions are right, cast iron will do a good job. [However,] if the least abrasion occurs, cast iron [will produce] a good grinding compound.

The use of serrated surfaces on the inside of the rings is ill advised because it necessitates a large number of rings and a long breaking-in period. Rather, the surfaces should be finished smooth and then be lapped to the piston. There should be no sharp edges which will prevent the lubricant from getting between the packing and the piston.

For good alignment there will be a floating connection between the piston and the crosshead, with a bushing on each side of the packing for piston support.

In [Figs. 5-30a and b and 5-28c] the lubrication is of the boundary type. In [Fig. 5-30c] is shown a packing whose performance depends upon hydrodynamic lubrication. It has long been known that a film of lubricant between moving surfaces is capable of retaining very high pressures, but it has been necessary to use a means of developing a lubricant pressure as high as the pressure to be retained. Although the theory and application of wedge action have been used for developing lubricant pressure in certain types of bearings the idea shown here is a new concept of the principle (U.S. Patent 2,369,883).

The packing element consists simply of a close-fitting bushing which has a rounded or tapered entrance at the outer or low-pressure end, where the lubricant is introduced at approximately suction pressure. Extremely high pressure can be produced by the wedge effect. For the establishment of a pressure film, the

film thickness must be variable, with the inlet thickness greater than the outlet thickness. . . .

With the lubricant being delivered at a constant low pressure, on the discharge stroke the wedge action builds up a film pressure between the plunger and the packing element which balances or exceeds the cylinder pressure. It has been demonstrated that lubricant at atmospheric pressure can be forced through a packing element against a pressure of 10,000 psi. On the suction stroke, the lubricant and the cylinder fluid are under balanced pressure conditions.

This packing is satisfactory for either liquids or gases. Improvements under consideration will increase the flexibility and extend the pressure range to anything that is commercially desired.⁴⁵

The packing arrangements used on 10,000-psi gas compressors and coal-paste injectors are described by Chaffee and Hirst.⁴⁷

The O ring may be used to seal a moving piston. This ring is inserted in a slot between the two surfaces to be sealed, as shown in Fig. 5-31a. The dimensions of this slot are carefully specified to provide a diametral squeeze on the O ring. As pressure is applied or as the slot is moved back and forth, the O ring fills the slight clearance and prevents leakage. It is claimed that this design will seal against pressures up to 1,500 psi for motion parallel to the shaft. For continuous rotary motion care must be exercised to provide good lubrication and cooling, since the heat generated by the contact between the rubber and metal must be dissipated.

The Bridgman unsupported-area principle described earlier may also be applied to packing a piston as shown in Fig. 5-31b. This is useful at pressures up to several thousand atmospheres. The end of the piston is made as a separate piece, and this acts on a ring of softer packing material having a smaller cross-sectional area than the end of the piston.

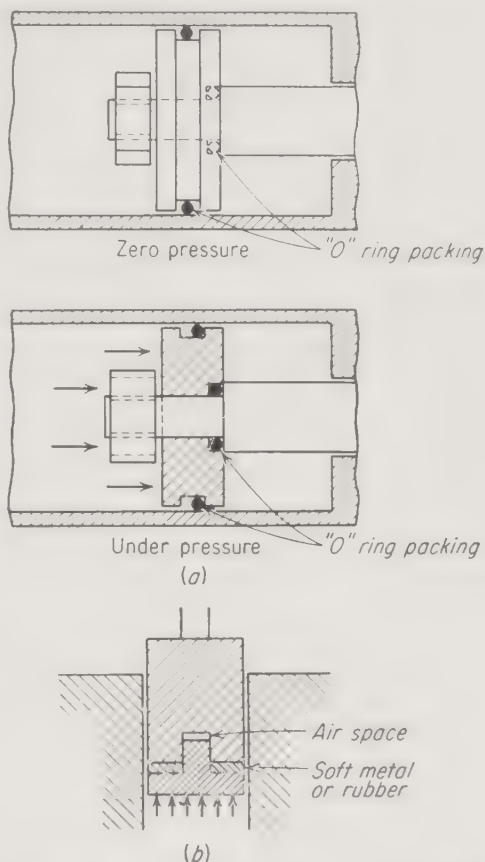


FIG. 5-31. Sealing a piston. (a) O-ring seal. (b) Bridgman packing.

⁴⁷ C. C. Chaffee and L. L. Hirst, *Ind. Eng. Chem.*, **45**:822 (1953).

This is achieved by allowing a portion of the end piece to extend through the soft packing. This portion of the area of the piston is not supported by the packing and results in a higher pressure in the packing material than is acting on the end of the piston. The packing material must be soft enough to transmit the pressure of the movable end of the piston radially to the walls of the cylinder and at the same time be sufficiently rigid that it does not flow into the clearance between the piston and cylinder. A very effective seal is provided, and the tendency to leak is independent of the pressure in the cylinder. The design is not readily adaptable to a reciprocating plunger as used in liquid pumps.

5-7. Compressors and Liquid Pumps. Gas compressors or liquid pumps are used when liquids or gases are subjected to high pressures. For pressures up to 5,000 psi, relatively standard designs are available in both large and small sizes. Designs for pressures up to 25,000 psi in laboratory sizes are also fairly standard. Large commercial compressors for pressures above 5,000 psi are especially designed for each installation. Such installations have been made for pressures up to 15,000 psi and higher. In the smaller sizes, reciprocating mechanical types have been built for pressures up to 60,000 psi; and those employing the hydraulic-intensifier principle, in some cases with hand-operated valves, can be used to 200,000 psi.

Gas Compressors. A discussion of the complete design, operation, and maintenance of gas compressors and pumps is not within the scope of this book. As the pressure increases, greater care is needed in designing certain parts of the compressor. The bearing surfaces, valves, piston packing, piston-rod stuffing boxes, and the proportioning of cylinder displacement between cylinders in a multistage compressor require special consideration. Maintenance also becomes a greater factor with increasing pressure, and the accessibility of parts becomes more important.

The compression of a gas to 15,000 psi is usually carried out in six or seven stages, while 5,000 psi is attained in about four stages and 1,000 psi in about three stages. The choice of the compression ratio per stage and the number of stages is important for continuous operation where the power costs are a large part of operating costs. The displacement in each stage depends largely on the pressure-volume-temperature relationships for the gas being compressed. The calculation of the displacement and the power requirements for each stage will be described.

In the smaller compressors, the several stages are assembled in one machine and the gas is raised from the low pressure to the high in one unit. These stages may be either in line on a single shaft or arranged to be driven by two or more cranks in a duplex or triplex arrangement. The large commercial installations frequently separate the several stages into two separate units. Compression at a constant temperature requires

less power than when the temperature is allowed to rise during compression. The compression in each stage, especially in the larger machines, tends to be adiabatic with a large rise in temperature. The addition of more stages permits intercooling with a closer approach to constant-temperature operation and a lower power requirement, but this advantage

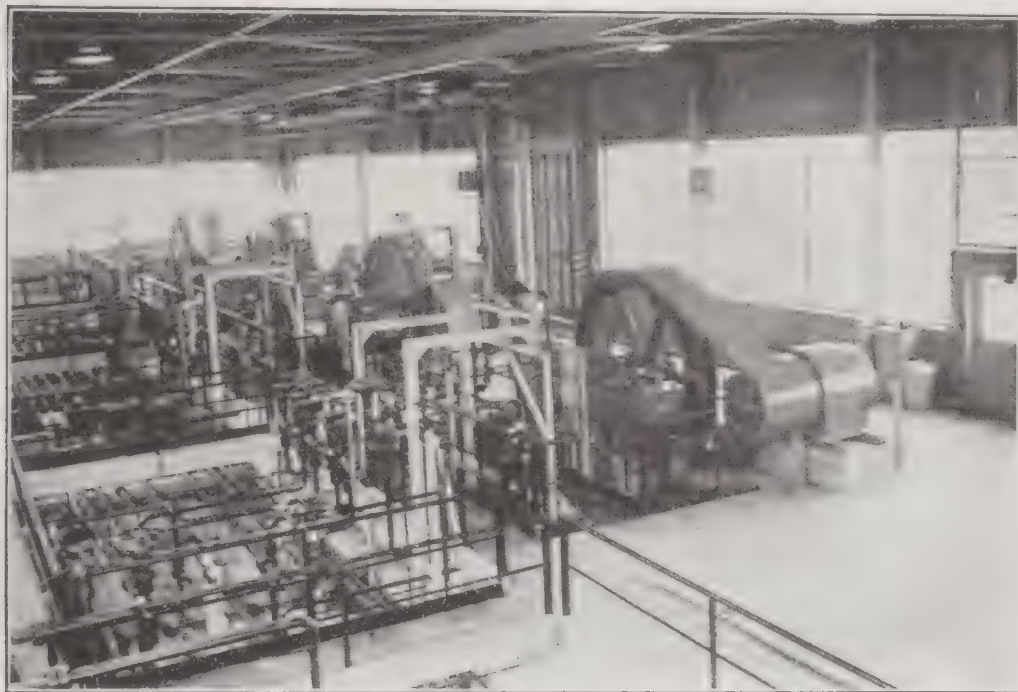


FIG. 5-32. High-pressure hydrogen-circulating compressors at Louisiana, Missouri. (From J. A. Markovits,⁴⁸ U. S. Department of the Interior, Bureau of Mines.)

is balanced by the increased first cost and maintenance of a larger number of stages.

An installation of a high-pressure hydrogen-circulating compressor⁴⁸ is shown in Fig. 5-32. The associated piping and high-pressure valves are shown in the foreground. Figure 5-33 shows a cross section through the fifth and sixth stages of a six-stage compressor discharging at 15,000 psi. In this case, the six stages are arranged on two compressor frames. On one end of one compressor frame is mounted the first-stage double-acting cylinder, and on the opposite end of the same frame are mounted the second- and third-stage cylinders, arranged in tandem. On one end of the other compressor frame is mounted the fourth-stage cylinder, which is single-acting. On the opposite end of the same frame are mounted, in tandem, the single-acting fifth- and sixth-stage cylinders. The fifth-stage piston acts in the inboard direction, and the sixth-stage piston acts in the outboard direction. The fifth and sixth stages are shown in the

⁴⁸ J. A. Markovits, *Trans. ASME*, **72**:349 (1950).

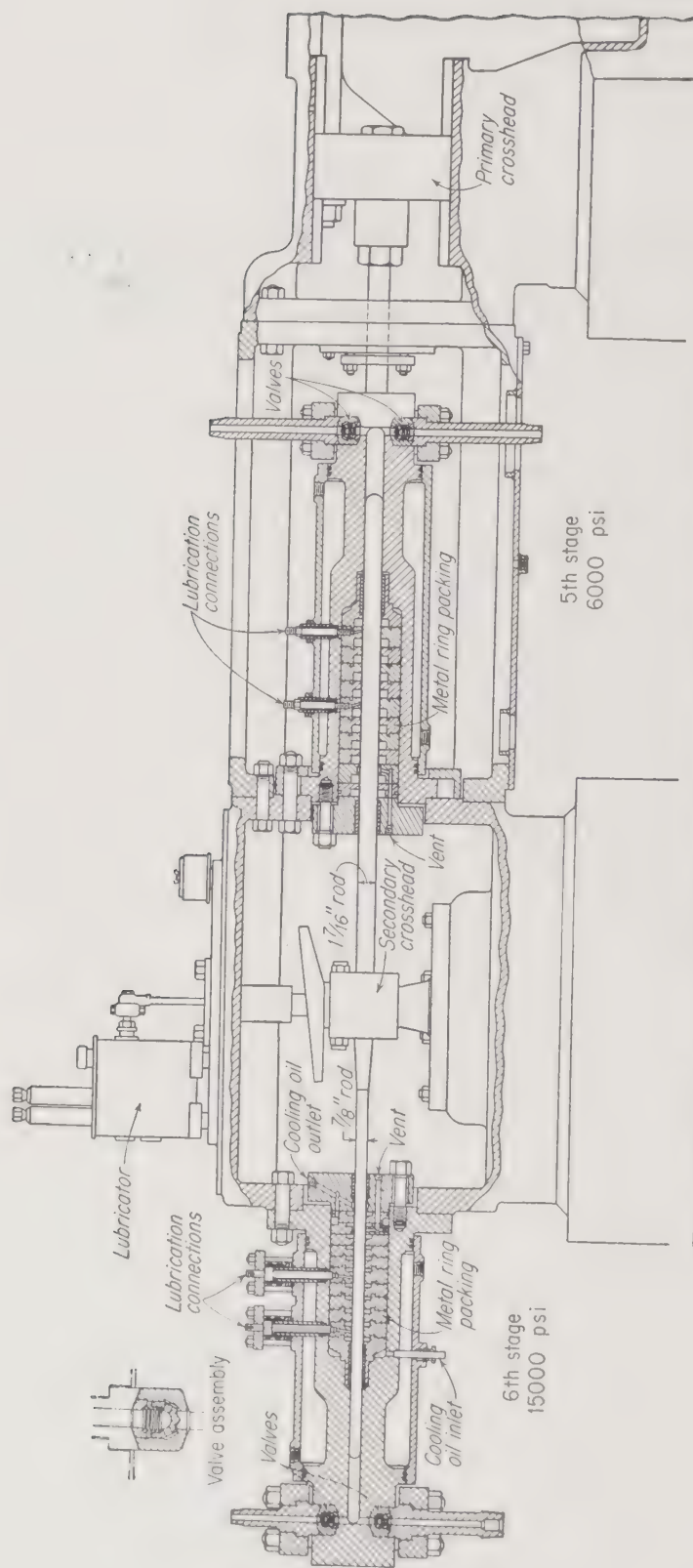


FIG. 5-33. Cross section of high-pressure stages. (Worthington Corporation.)

illustration. These stages are equipped with plate-type valves similar to those shown in Fig. 5-37. The pistons are packed with metal rings.

In the smaller-size compressors, the Rix type K gas compressor shown in Fig. 5-34 is typical of those for service up to 5,000 psi. This compressor has a capacity of 12 cu ft/min of free air and is constructed

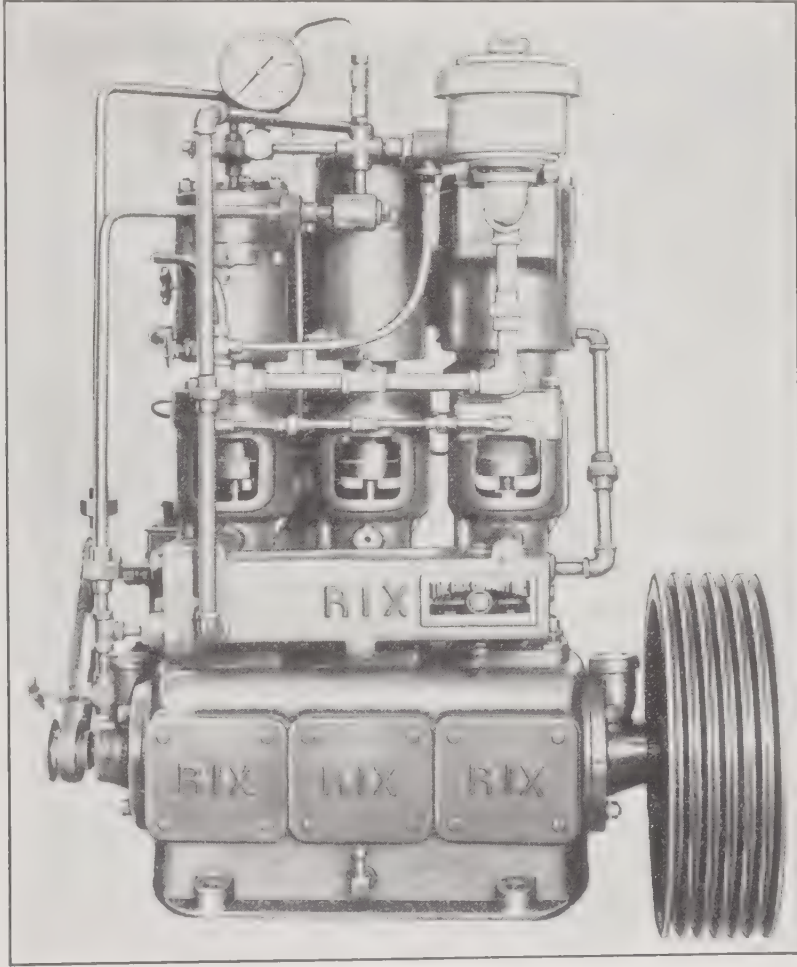


FIG. 5-34. Rix type K gas compressor—three stages. (*American Instrument Company.*)

with three stages, each driven from a separate crank on the main crankshaft. The speed range is from 350 to 600 rpm requiring from 5 to 10 hp.

Several sizes of gas compressors for pressures up to 15,000 psi and capacities ranging from 0.6 to 30 cu ft/min are manufactured by Andreas Hofer of Mulheim-Ruhr. One of the smallest of these is shown in Fig. 5-35. This compressor has a capacity of 6 cu ft/min of free gas and operates at 300 rpm. The delivery pressures from the five stages are 38, 150 to 220, 900 to 1,200, 3,800 to 4,200, and 15,000 psi. The five pistons are arranged along a shaft in a single line and are driven by a

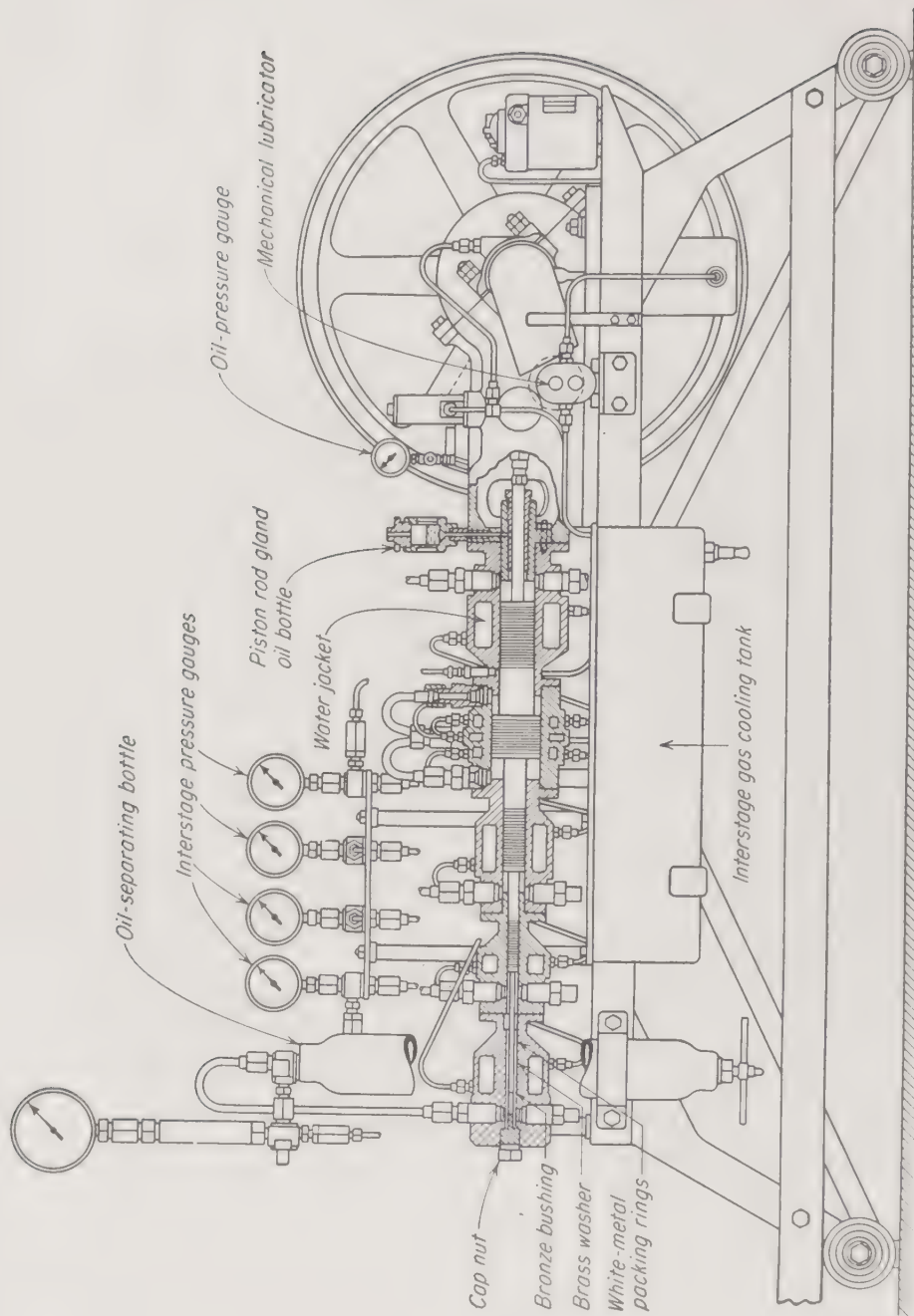


FIG. 5-35. Hofer 1,000-atm compressor—five stages. (H. Tongue, "The Design and Construction of High Pressure 'chemical Plants,'" Chapman & Hall, Ltd., London, 1931, and Autoclave Engineers Inc.)

single crank. Beginning at the crank end, the stages are in the order second, first, third, fourth, and fifth stages. The first stage is double-acting, and all the rest are single-acting. The pistons of the first four stages are fitted with piston rings, while the fifth stage is of the plunger type and is sealed by packing placed around it. This packing consists of white-metal rings held in place by a long bronze bushing which is pressed against the rings by a cap nut. The packing is adjusted by inserting thin-brass-washer shims, 0.002 to 0.003 inches thick, between the white-metal rings and the bronze bushing.

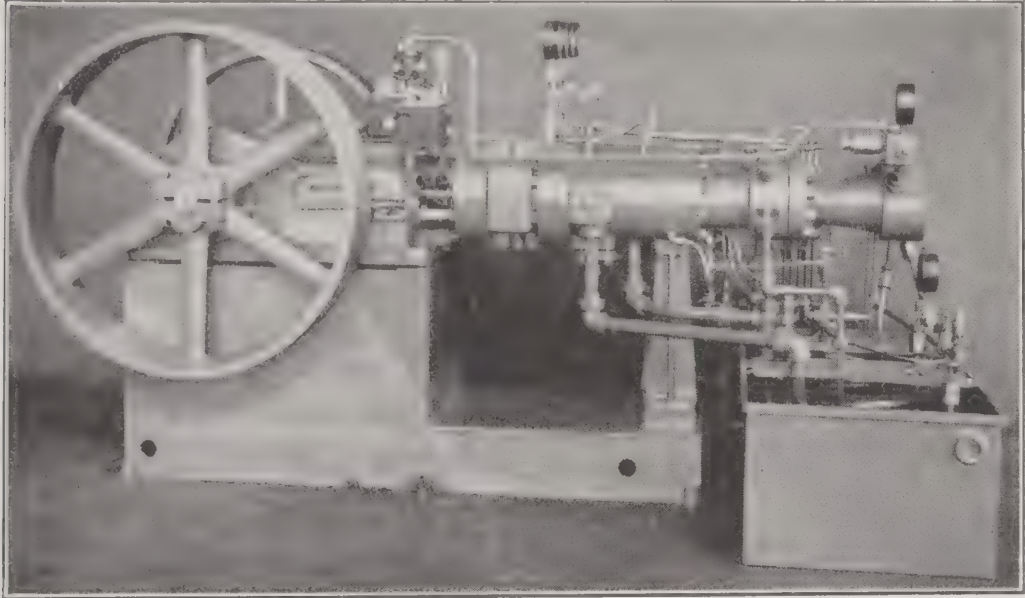


FIG. 5-36. Norwalk compressor—25,000 psi. (Norwalk Company, Inc.)

The second stage is placed next to the piston-rod packing gland, thus ensuring that the latter will always be subjected to a positive internal pressure so that leakage of air into the system is prevented. This packing gland is provided with an oil-lantern ring, lubricated from an oil chamber which is connected to the second stage, and maintained under the same gas pressure. Each cylinder is water-jacketed, and the gas from each stage is passed through copper coils in a water-cooling tank before entering the next stage. All the pistons are lubricated by oil entrained in the first cylinder and carried through to the other pistons. The gas from the fifth stage then enters a separating bottle where oil and water are removed from it.

A small gas compressor for similar service is shown in Fig. 5-36. This is built by the Norwalk Company and consists of six stages mounted in duplex with a capacity of 5 cu ft/min. The compressor operates at about 150 rpm and has a maximum pressure of 25,000 lb/sq in. requiring a 15-hp motor. These stages are arranged with the second-stage, fourth-

stage, and sixth-stage cylinder mounted on one side and the first, third, and fifth stages mounted on the other. The first stage is double-acting, and all the rest are single-acting. The first four stages have pistons equipped with piston rings, while the fifth- and sixth-stage pistons are of the packed-plunger type. The piston rings in the first and second cylinders are cast iron, while those in the third and fourth are the double-seal

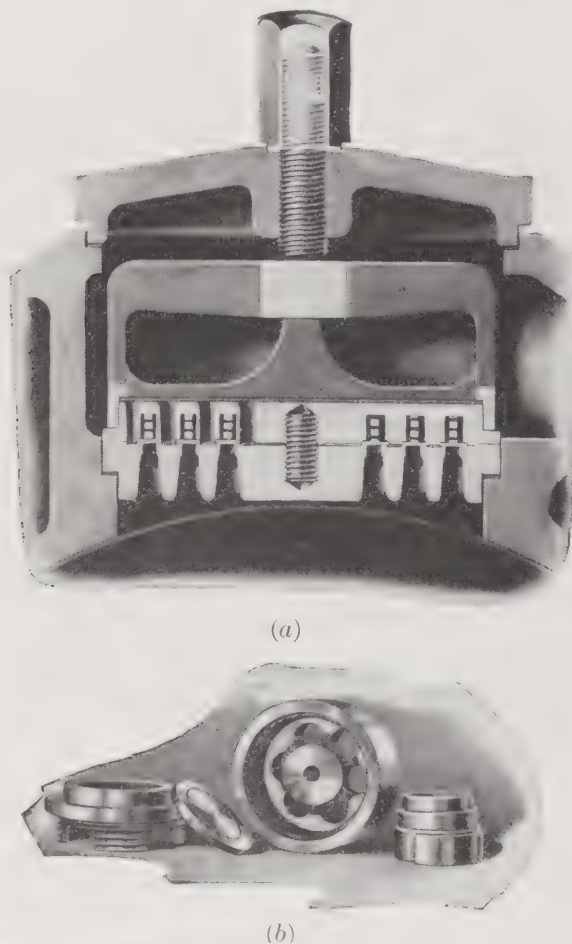


FIG. 5-37. Ring-plate valves used in Norwalk compressor. (Norwalk Company, Inc.)

ring type. The valves are of the ring-plate-and-disk type, which provides a large area and low lift for long wear and silent operation. The assembled valve is shown in Fig. 5-37a. The three rings are valve plates which are held down lightly on the valve seats by the three-coiled springs. These valve plates are carefully lapped to ensure a perfect seat. The complete valve assembly is interchangeable either as an intake or discharge valve depending upon which side is located next to the cylinder. Typical valve parts are shown in Fig. 5-37b. A coil-and-tank-type inter-cooler is used between stages.

The gas at about 15,000-psi pressure from one of the above units

may be further compressed in a single-stage unit. A single-stage compressor of this type which will raise the pressure to 30,000 psi is supplied by Hofer. Burekhardt in Switzerland supplies a single-stage compressor with hydraulic drive and completely automatic operation which takes suction at 1,000 atm and delivers at 60,000 psi. This is shown in Fig. 5-38. It has a capacity of 12 liters/hr at suction conditions. A similar

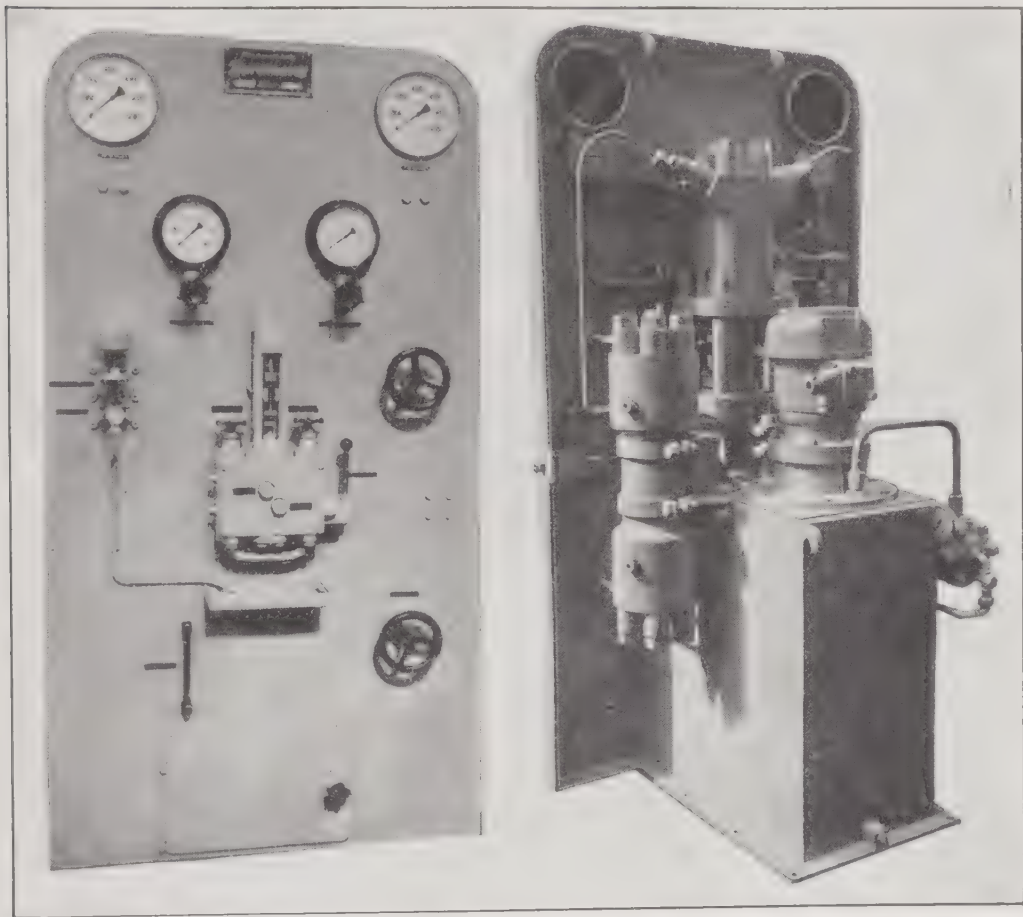


FIG. 5-38. Burekhardt single-stage compressor for 60,000 psi—front view and rear view. (*Burekhardt Engineering Works, Basle, Switzerland.*)

unit for 100,000 psi is under construction. Burekhardt also manufactures a five-stage 1,000-atm compressor with a capacity of $42\frac{1}{2}$ cu ft/hr. A five-stage gas compressor built by Hofer is shown in Fig. 5-39.

When high-pressure gases are to be recycled, as through the reactor in the synthetic-ammonia process, a gas-circulating pump is required. This is designed to withstand the maximum pressure in the system, although the compression ratio need not be high. Its function is to recompress the gas through a pressure change equivalent to the pressure drop through the piping and reactor.

Hydraulic Intensifier. Gas under an initial high pressure may be further compressed in a hydraulic intensifier. Such a device is shown in Fig. 5-40. This consists of two pistons connected to the opposite ends of a shaft with one piston having a larger area than the other. Oil is pumped into the large cylinder, forcing its piston to drive the smaller piston. The large piston is readily packed with leather cup-type packing since the pressure is not high, and the seal is against oil rather than against a gas. The small piston is carefully lapped to close tolerances

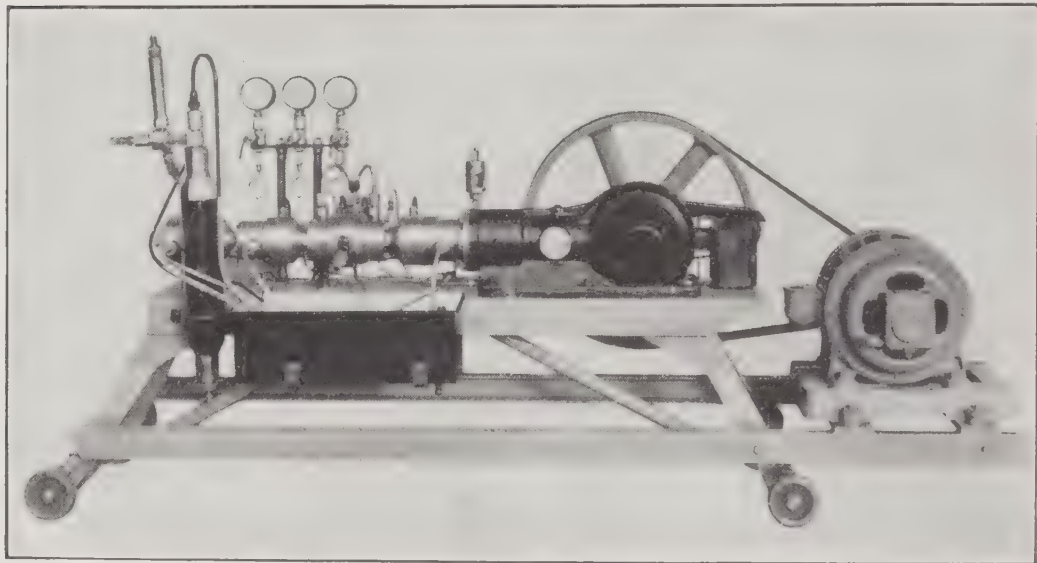


FIG. 5-39. Hofer high-pressure gas compressor. (*Autoclave Engineers Inc.*)

and is provided with a packing of the unsupported-area type. The hydraulic intensifier shown in the figure is built by the Harwood Engineering Company and is designed for a pressure of 200,000 psi. The pump and tubing connecting it to the low-pressure cylinder are shown, and the small-diameter high-pressure piston is visible in the circular opening. The height is 5 ft 8 in.

The hydraulic-drive principle has been used in large-capacity compressors. The Sulzer 1,000-atm gas compressor is described by Tongue.⁴⁹ It is designed to handle 2,500 cu ft/min with a discharge pressure of about 15,000 psi. This is a seven-stage compressor with the first five stages driven mechanically in a conventional manner by a drive shaft. The sixth and seventh stages are of a plunger type and are driven by hydraulic pistons. These, in turn, are actuated by a piston on the main drive shaft. The arrangement is shown diagrammatically in Fig. 5-41. An oil pipe *a* connects the primary piston *b* on the main shaft directly

⁴⁹ Harold Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman & Hall, Ltd., London, 1934.

to each of the secondary, hydraulically operated pistons *c* and also connects the two secondary pistons. Each of the oil columns is equipped with a safety valve. This protects these two stages from damage in the event that the plungers become tight or stick in the cylinders. These hydraulically driven plungers are free bodies and have no mechanical connection with the rest of the system. This arrangement assists in

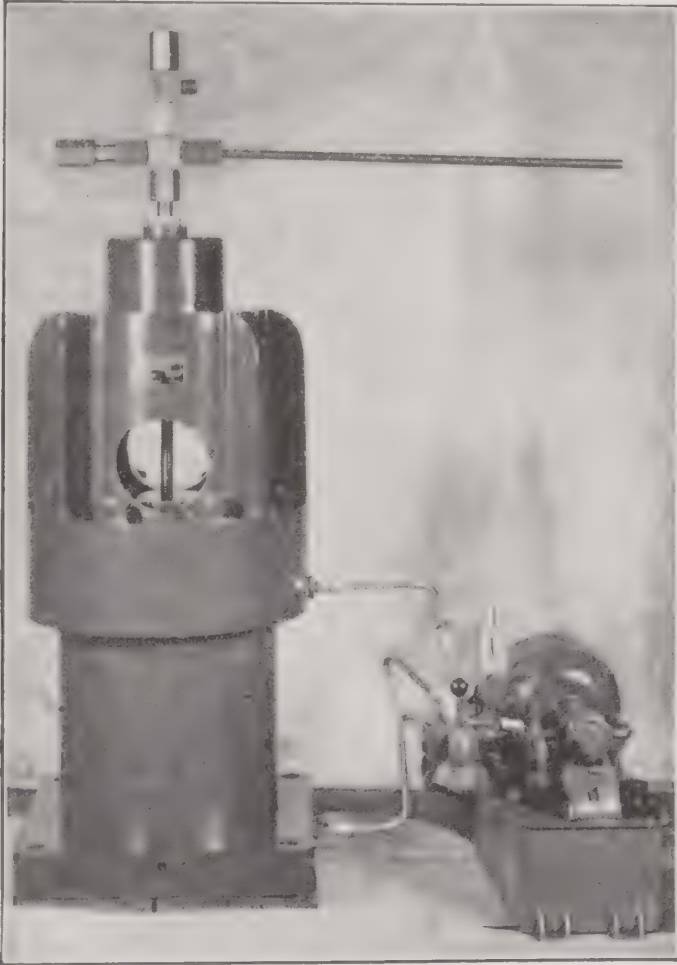


FIG. 5-40. Hydraulic intensifier. (*Harwood Engineering Company, Inc., Walpole, Mass.*)

maintaining perfect alignment during the whole stroke and avoids wear on the packing, which usually remains in good condition for approximately 3,000 hr of service without requiring attention.

A piston utilizing a packing based on Bridgman's unsupported-area principle may be used for pressures possibly approaching 300,000 psi. This design is limited not so much by its ability to prevent leaks as by the strength of the stem which projects into the unsupported-area portion of the piston. At high radial pressures, this stem tends to be pinched off.

An intensifier using a piston incorporating this design is shown in Fig. 5-42.

In precise experimental work, a gas that has been carefully purified should be compressed without bringing it into contact with lubricating oil and packing materials encountered in the usual compressors. A device which brings the gas into contact only with the metal walls of the

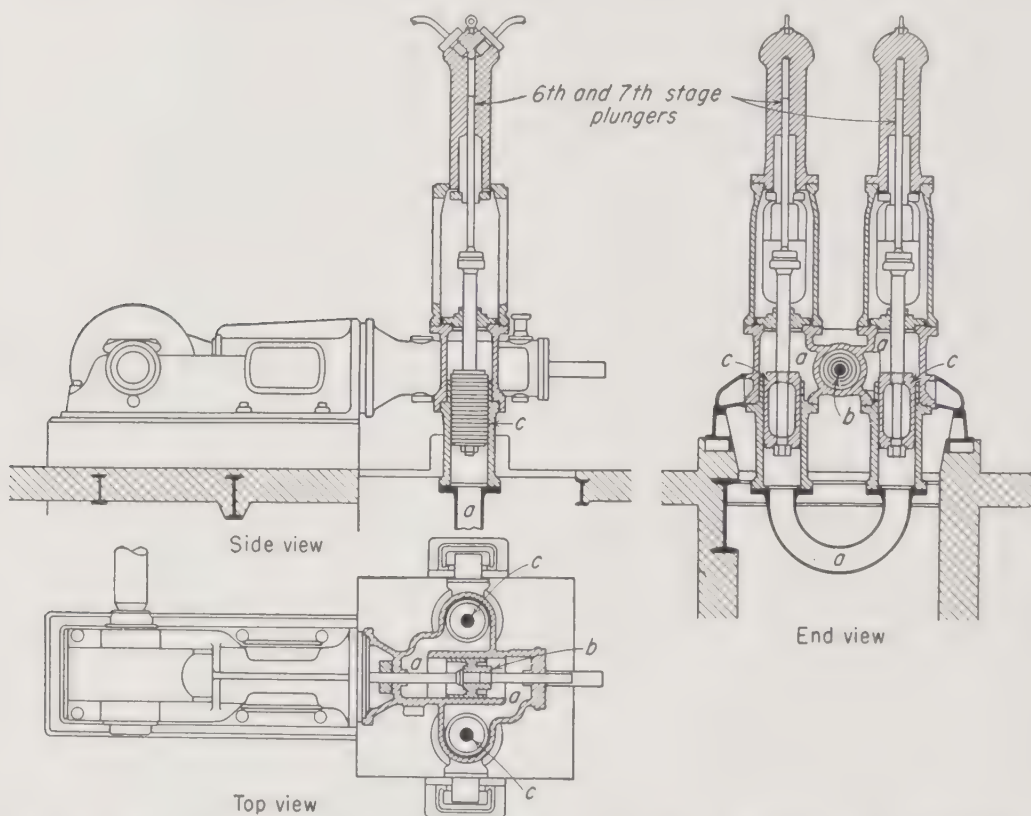


FIG. 5-41. Sulzer hydraulically driven compressor. (From H. Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman & Hall, Ltd., London, 1931.)

compressor and with mercury has been designed by Michels⁵⁰ and is shown in Fig. 5-43. This compressor consists of two chambers. The lower chamber is filled with mercury, and pressure is then applied to the top of the mercury by introducing oil into the chamber. The mercury flows up through a riser tube to the upper chamber. By introducing oil under high pressure from a hydraulic pump, this pressure is transmitted to the mercury in the lower chamber and thence to that in the upper chamber. The gas to be compressed is introduced above the mercury in the upper chamber and is compressed as the mercury rises. Continuous operation requires that the proper valves be manipulated by hand.

⁵⁰ W. C. 'tHart & Zn., Rotterdam.

Design of Gas Compressors. In preparing specifications for a gas compressor, the inlet temperature and pressure and the outlet pressure are usually known. The number of stages must then be selected, and, in this connection, the exit temperature from each stage and the work of compression in each stage are calculated. Compressor operation is usually not adiabatic and thermodynamically reversible (isentropic), but calculations on this basis are likely to be accurate enough to serve as a sound estimate of performance. This estimate is subject to adjustment

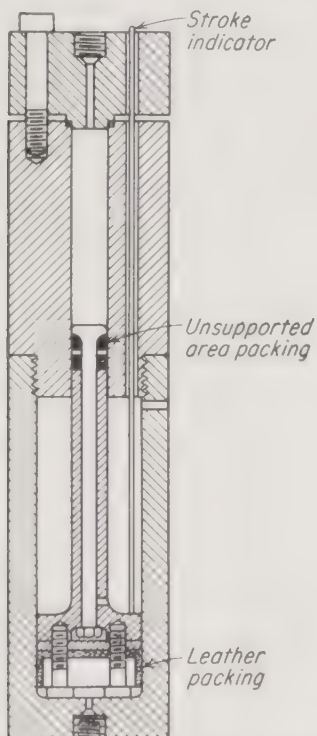


FIG. 5-42. Piston with Bridgman packing. (American Instrument Company, Inc.)

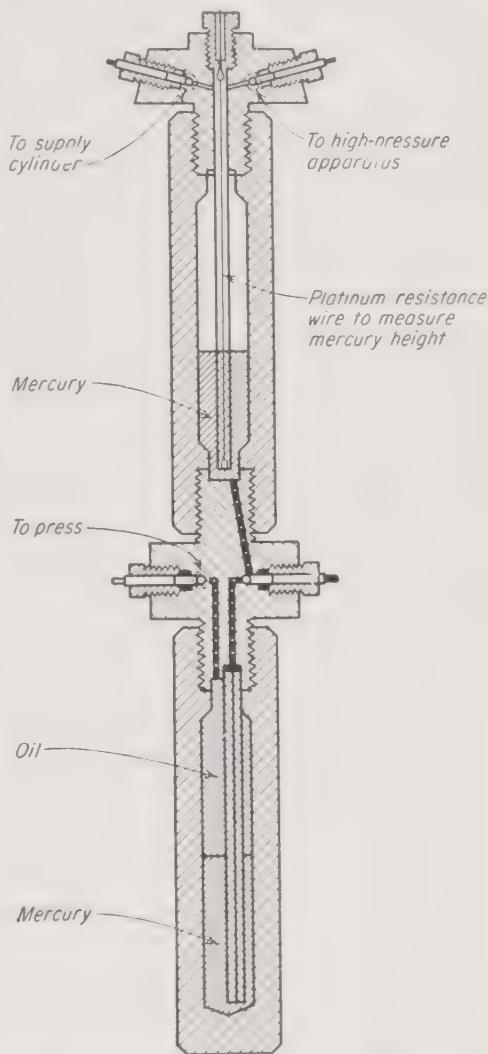


FIG. 5-43. Michels mercury-piston gas compressor. (From H. Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman & Hall, Ltd., London, 1931.)

resulting from the manufacturer's experience with specific designs. Calculations on this basis will be made in the following examples.

At relatively low pressures and for most of the permanent gases, use of equations based on the perfect-gas laws is justified. In such cases, the ratio of outlet to inlet temperatures for isentropic compression is given by

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{(\gamma - 1)/\gamma} \quad (5-11)$$

The theoretical work of isentropic compression in each stage for a flow process is

$$W_c = \frac{\gamma}{\gamma - 1} p_1 v_1 \left[\left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (5-12)$$

At higher pressures and for gases at temperatures in the vicinity of their critical temperature, the deviations from the perfect-gas laws are large and render the above equations seriously in error. Calculations can then be based on the measured pVT relations and the heat capacity of the gas under consideration. This information can be most readily used when it is in the form of thermodynamic tables or charts such as the Mollier diagram in common use for steam. The methods for using these charts to calculate changes in temperature and the theoretical work involved in isentropic compression are adequately described in standard texts on thermodynamics.⁵¹

Thermodynamic charts and tables are available for a few substances including steam, oxygen, nitrogen, air, hydrogen, helium, carbon dioxide, sulphur dioxide, ammonia, methane, ethane, propane, butane, and some halogen derivatives of methane and ethane. The isentropic work of compression between an initial state A and a final state B may be read from these thermodynamic charts directly as a change in enthalpy by following a constant-entropy line. When charts are not available, an estimate of the change in enthalpy may be obtained from generalized correlations. York⁵² describes a calculation by successive approximation employing a generalized correlation of entropy as a function of reduced pressure and reduced temperature. A suitable correlation is shown in Fig. 8-22. The temperature and pressure are usually known for the initial state, but only the pressure for the final state. The calculation is made by first selecting a final temperature as an estimate. This temperature determines a final state B . The change in entropy is calculated along a convenient equivalent path such as the following: (a) reduce the pressure to 1 atm at constant temperature, (b) heat the gas at low pressure to the final temperature, and (c) raise the pressure at the final temperature from 1 atm to the final pressure. This three-step path is illustrated in Fig. 5-44. The initial state is shown at A , and the estimated final state at B . Since the entropy and enthalpy changes are independent of the path of the process, the change in these values between A and B is the same for all paths. The change in entropy thus calculated should be zero, or the estimate of the final temperature is not correct. Another final temperature must then be chosen and the calculation repeated

⁵¹ B. F. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1944.

⁵² Robert York, Jr., *Ind. Eng. Chem.*, **34**:535 (1942).

until the entropy change is zero. The selection of the correct final temperature may be facilitated by plotting the estimated temperature versus the change in entropy and extending the resulting curve to zero entropy change.

With the final temperature established, the next step consists of evaluating the change of enthalpy along the same path. This calculation uses a generalized correlation of ΔH for changes in pressure at constant volume.

Example 5-1. Calculate the work of compression when gaseous propane is compressed isentropically from 80°F and 100 psi to 400 psi.

$$p_{R_1} = \frac{100}{14.7 \times 42.0} = 0.162$$

$$T_{R_1} = \frac{540}{666} = 0.813$$

$$p_{R_2} = \frac{400}{14.7 \times 42.0} = 0.648$$

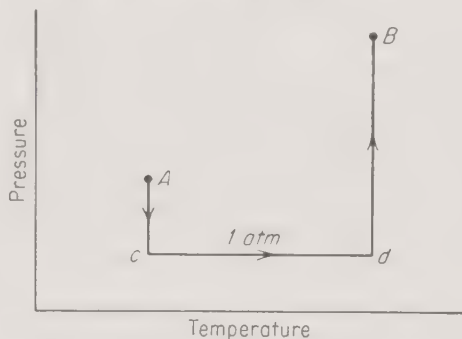


FIG. 5-44. Three-step path for evaluating ΔS and ΔH .

The heat capacity of propane gas as given by Edmister⁵³ may be represented by

$$C_p = 4.09 + 0.0240T$$

Try $T_2 = 655^\circ\text{R}$.

The entropy at A (Fig. 5-44) below that of an ideal gas is found from Fig. 8-22 to be

$$S_i - S = -0.80$$

Adding the entropy change of an ideal gas from A to c,

$$(\Delta S_i)_{Ac} = 1.987 \ln \frac{100}{14.7} = 3.81$$

From c to d,

$$\begin{aligned} (\Delta S_i)_{cd} &= \int_{540}^{655} (4.09 + 0.0240T) \frac{dT}{T} \\ &= 4.09 \ln \frac{655}{540} + 0.024(655 - 540) = 3.54 \end{aligned}$$

From d to B for an ideal gas,

$$(\Delta S_i)_{dB} = -1.987 \ln \frac{400}{14.7} = -6.58$$

For the real gas, $T_{R_2} = \frac{655}{666} = 0.98$,

$$\begin{aligned} (S - S_i)_B &= -1.60 \\ \Delta S_{BA} &= -0.03 \end{aligned}$$

Thus 655°R is the correct value of T_2 . If ΔS_{BA} was not zero, a new value of T_2 should be chosen.

⁵³ W. C. Edmister, *Ind. Eng. Chem.*, **30**:352 (1938).

The change in enthalpy $H_B - H_A$ may now be calculated. From Fig. 8-19, $(H_c - H_A)/T_c = 0.82$.

$$H_c - H_A = 0.82 \times 666 = 545$$

$$\begin{aligned} H_d - H_c &= \int_{540}^{655} (4.09 + 0.024T) dT \\ &= 4.09(655 - 540) + \frac{0.024}{2} (655^2 - 540^2) = 2125 \end{aligned}$$

and $(H_B - H_d)/T_c = -2.2$.

$$\begin{aligned} H_B - H_d &= -2.2 \times 666 = -1465 \\ H_B - H_A &= 1205 \text{ Btu/lb mole} \end{aligned}$$

Edmister and McGarry⁵⁴ propose another method of calculating the final temperature based on a generalized correlation. This method does not require successive approximations, but it is less rigorous than York's method. An expression for the isentropic change in temperature between pressures p_1 and p_2 is written as

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{\Phi}{C_p}} \quad (5-13)$$

The change in entropy for an actual gas is given by

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_p dp \quad (5-14)$$

For a change at constant entropy, $dS = 0$ and

$$\frac{dT}{T} = \frac{1}{C_p} \left(\frac{\partial v}{\partial T} \right)_p dp \quad (5-15)$$

From the definition of the generalized compressibility factor, $z = pv/RT$

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} \left[z + T \left(\frac{\partial z}{\partial T} \right)_p \right] \quad (5-16)$$

Combining Eqs. (5-15) and (5-16) and integrating between T_1, p_1 and T_2, p_2 along an isentropic path gives

$$\int_{T_1}^{T_2} \frac{dT}{T} = \int_{p_1}^{p_2} \frac{R}{C_p} \left[z + T \left(\frac{\partial z}{\partial T} \right)_p \right] \frac{dp}{p} \quad (5-17)$$

The integration may be readily carried out if the term $(R/C_p)[z + T(\partial z/\partial T)_p]$ is considered constant. With this restriction and representing this term by Φ/C_p , Eq. (5-17) gives Eq. (5-13). This reduces to Eq. (5-11) when $z = 1$, as for an ideal gas. The term Φ/C_p is not constant for actual gases for appreciable changes. Equation (5-13) is rigorous if T_2 and p_2 are close to T_1 and p_1 and both z and C_p may be considered

⁵⁴ W. C. Edmister and R. J. McGarry, *Chem. Eng. Progr.*, **45**:421 (1949).

constant. When T and p vary over a greater range the equation is not rigorous, but Edmister and McGarry recommend that an arithmetic average of Φ/C_p evaluated at the initial and final conditions be employed. This recommendation is based on their experience with 72 calculations in

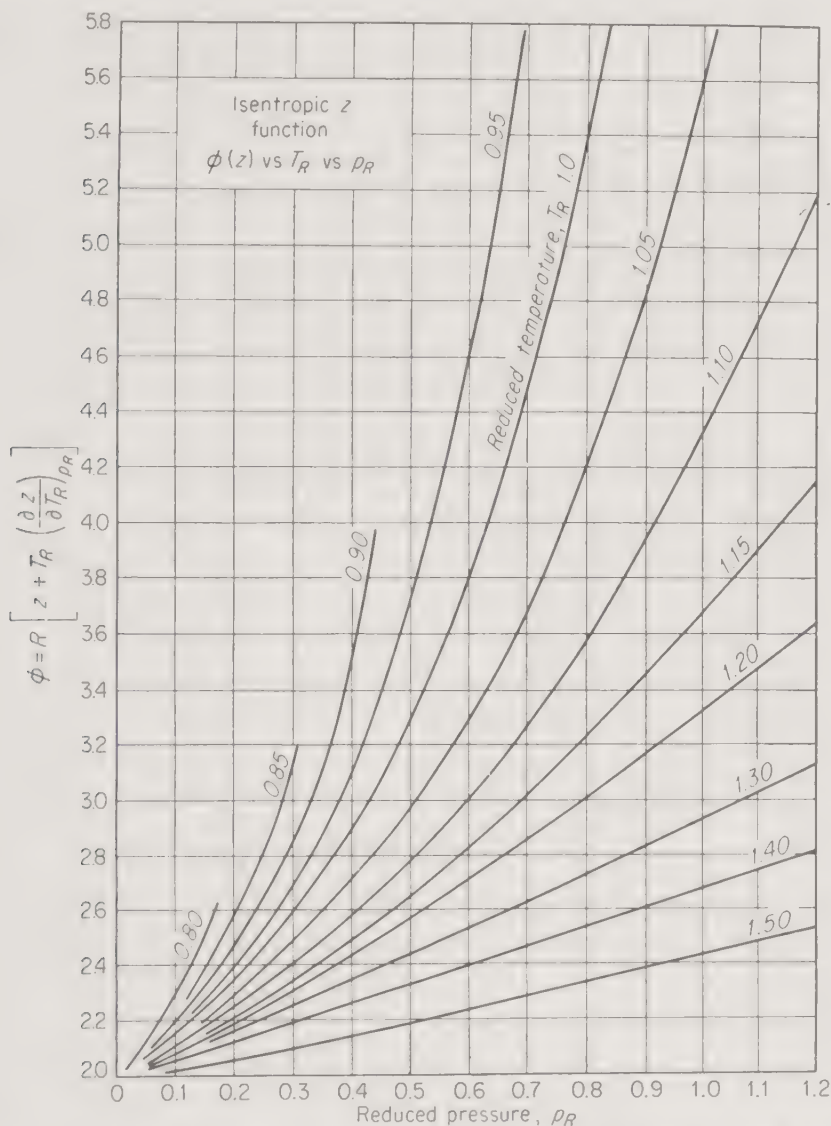


FIG. 5-45. Generalized correlation of $R[z + T_R(\partial z/\partial T_R)_{p_R}]$ vs. T_R and p_R . [From W. C. Edmister and R. J. McGarry, *Chem. Eng. Prog.*, **45**:421 (1949).]

which this empirical rule is compared with rigorous calculations using thermodynamic charts. They conclude that the rule is satisfactory. A generalized correlation of Φ is presented as a function of reduced temperature and reduced pressure. This correlation is shown in Fig. 5-45.

Example 5-2. Edmister's method uses three generalized thermodynamic correlations. These are shown in Figs. 5-45, 8-19, and 8-20. As an example, consider the isentropic compression of ethylene at 0°F and 147 psia to 882 psia, and calculate the final temperature and the work of compression.

$$\begin{aligned}T_{R_1} &= 460/510 = 0.90 \\p_{R_1} &= 147/49 = 0.196 \\C_{p_1}^* &= 9.42 \text{ (see Appendix D)}\end{aligned}$$

From Fig. 8-20, $\Delta C_{p_1} = 2.60$

$$C_{p_1} = 9.33 + 2.60 = 11.93$$

From Fig. 5-45, $\Phi_1 = 2.46$

$$\frac{\Phi_1}{C_{p_1}} = \frac{2.46}{11.93} = 0.205$$

This value of Φ_1/C_{p_1} may be used in Eq. (5-13) to obtain an estimate of the final temperature. Thus $T_2 = 460(882/147)^{0.205} = 665^\circ\text{R} \approx 205^\circ\text{F}$. This value of T_2 may be used to obtain a more accurate value as follows,

$$\begin{aligned}T_{R_2} &= 665/510 = 1.30 \\p_{R_2} &= 882/49 = 1.18 \\\Phi_2 &= 3.12 \\C_{p_2}^* &= 12.22 \\\Delta C_{p_2} &= 5.00 \\C_{p_2} &= 12.22 + 5.00 = 17.22 \\\frac{\Phi_2}{C_{p_2}} &= \frac{3.12}{17.22} = 0.181 \\\left(\frac{\Phi}{C_p}\right)_{\text{av}} &= \frac{0.205 + 0.181}{2} = 0.193 \\T_2 &= 460 \times 6^{0.193} = 651^\circ\text{R} \approx 191^\circ\text{F}\end{aligned}$$

This compares with 210°F obtained from the measured values of York and White,⁵⁵ or an error in the calculated temperature change of 9.0 per cent.

The change in enthalpy is calculated as follows. From Fig. 8-19

$$\begin{aligned}-\left(\frac{\Delta H}{T_c}\right)_1 &= 0.70 \\-\left(\frac{\Delta H}{T_c}\right)_2 &= 1.90 \\C_{p, \text{mean}}^* &= 10.65 \\C_{p, \text{mean}}^* \Delta T &= 10.65 \times 191 = 2040 \\-\Delta H_{\text{net}} &= -(1.90 - 0.70)510 = -613 \\W_c &= 2040 - 613 = 1427 \text{ Btu/lb}\end{aligned}$$

When the final temperature is obtained, the work of compression may be calculated from the change in enthalpy as described above.

⁵⁵ R. York, Jr., and E. F. White, *Trans. Am. Inst. Chem. Eng.*, **40**:227 (1944).

A rigorous method for calculating the isentropic temperature and work of compression, using an equation of state, is given by Prausnitz.^{55a}

Selection of Interstage Pressures. A rigorous derivation of a criterion for the selection of interstage pressures for the compression of actual gases with isentropic compression in each stage and interstage cooling has been given by Elrod.⁵⁶ Consider a simple two-stage process without

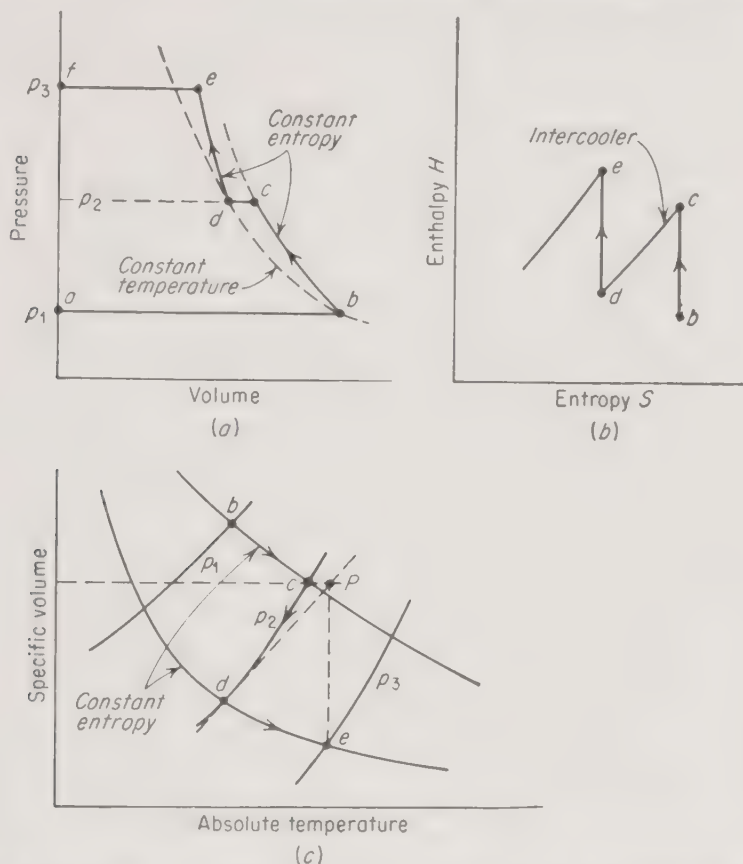


FIG. 5-46. Diagrams of two-stage compression with interstage cooling.

clearance, as illustrated in Fig. 5-46a, in which the gas passes through the cycle *abcdef*. The theoretical work of compression from Fig. 5-46b is given by

$$W_c = H_e - H_d + H_c - H_b \quad (5-18)$$

The minimum work with respect to changes in the value of the interstage pressure p_c is given by

$$dW_c = dH_e - dH_d + dH_c - dH_b \quad (5-19)$$

In this case, H_e varies at constant pressure p_3 , H_d varies at constant

^{55a} J. M. Prausnitz, *Ind. Eng. Chem.*, **47**:1032 (1955).

⁵⁶ H. G. Elrod, Jr., *Ind. Eng. Chem.*, **37**:789 (1945).

temperature T_d , H_c varies at constant entropy $S_c = S_b$, and H_b is fixed. Thus

$$dW_c = \left[\left(\frac{dH_e}{dS} \right)_p \left(\frac{dS_d}{dp} \right)_T - \left(\frac{dH_d}{dp} \right)_T + \left(\frac{dH_c}{dp} \right)_S \right] dp_3 = 0 \quad (5-20)$$

where the subscript in each of the numerators indicates the position of the derivative in the compression cycle. By substituting standard thermodynamic relations in this equation and rearranging, there results

$$\frac{v_c - v_d}{T_e - T_d} = \left(\frac{dv_d}{dT} \right)_p \quad (5-21)$$

This equation as derived by Elrod may be applied to the specific volume-temperature curves shown in Fig. 5-46c by a simple graphical construction and used to calculate the interstage pressure $p_2 = p_c$. Let the gas be cooled in the intercooler to the initial temperature. Then p_b , v_b , T_d , and p_e are specified, and it is required to calculate $p_c = p_d$. This is accomplished by a simple trial-and-error graphical procedure. Select a trial value of p_c . This fixes the conditions at c , d , and e (Fig. 5-46c). Now draw a tangent to the constant-pressure line at point d . The intersection of this tangent with the horizontal line through v_c determines the point P . If p_c has been chosen correctly, P will have the same temperature ordinate as position e . If it does not, new values of p_c must be chosen until the points P and e are on the same vertical line. If the isobar connecting c and d is a straight line, then T_e is the same as T_c . This is the situation with a perfect gas and also for the majority of real gases when the gas discharged from the intercooler is well removed from saturation and contains considerable superheat. The same type of graphical construction is correct if the gas is not intercooled to the initial temperature.

The total power requirement is not very sensitive to the selection of the interstage pressure, and the use of an interstage pressure which is the geometric mean of the two terminal pressures (correct only for perfect gases) will not seriously affect the design. The above procedures are readily extended to calculations for multiple stages.

Design for Actual Conditions. The design of a gas compressor for high-pressure service involves the selection of materials for the various parts, the design of these parts for proper performance, and a careful analysis of the arrangement of cylinders, valves, and driving mechanism. Such a design is outside the scope of this book. The methods which have been described permit making allowance for variations in the properties of the gases but not for variations in the mechanical design of the compressors. York⁵² discusses methods for adjusting the calculations for clearance between the piston and the cylinder head, for pressure

drops through the inlet and exhaust valves, and for leakage by the valves and pistons. These factors affect the volumetric efficiency of the compressor.

As a rule, a perfect gas requires a greater power consumption per mole for compression between fixed terminal pressures than an actual gas.

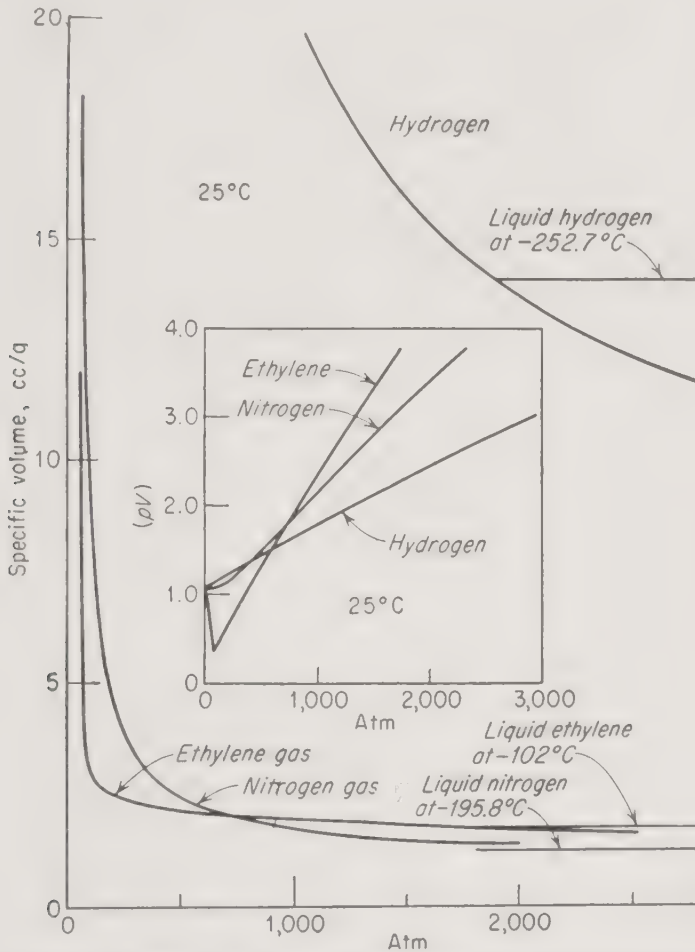


FIG. 5-47. Specific volume of three gases at high pressures.

The behavior of real gases is such as to require less power for compression. Deviations from this rule are to be expected in only two situations: (a) for low-molecular-weight gases, and adequate thermodynamic data are available for predicting their behavior, and (b) for most gases at pressures greater than ten times their critical pressure. In the latter case, the volume change on compression from one pressure to another is relatively small and the compressor acts more nearly like a liquid pump with most of the power being used to cause flow into and out of the cylinders, rather than to supply energy for compression.

Liquefaction. The compression of the permanent gases at relatively low pressures involves handling a highly compressible fluid. As another extreme and under other conditions, a more dense, incompressible fluid is handled. Such a dense phase results from compressing any gas to a sufficiently high pressure, from compressing or cooling a condensible

gas to its saturation conditions, or from compressing or cooling a gas mixture to its saturation conditions.

The first case is illustrated in Fig. 5-47 which shows the specific volume of hydrogen, nitrogen, and ethylene at 25°C as it varies with pressure. Also shown on the figure is the specific volume of these liquids near their boiling point. In each case the specific volume of the gas has been reduced to approximately that of the liquid at a pressure of 2,000 atm. The specific volume of the hydrogen approaches that of the liquid gradually as the pressure is increased, and that of the ethylene approaches it at relatively low pressures, having been reduced to twice the specific volume of the liquid at 80 atm. The pV product for each of these gases at 25°C as a function of pressure is also shown in Fig. 5-47. The three gases cover a typical range of behavior of pure gases.

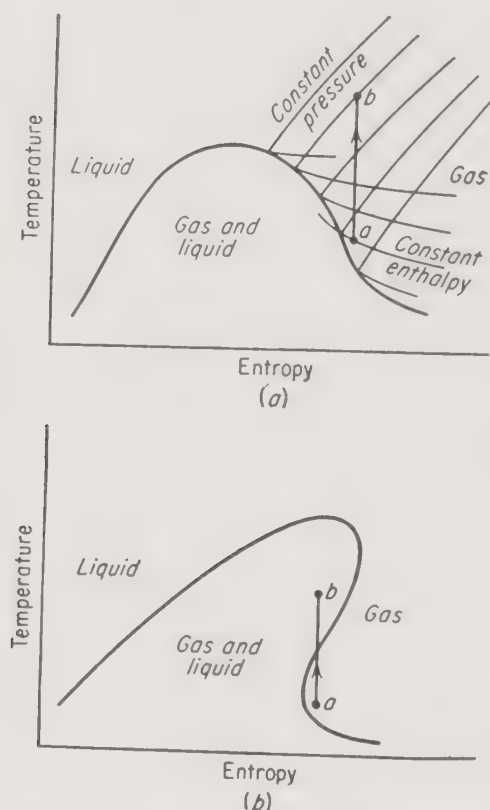


FIG. 5-48. Temperature-entropy diagrams for two gases.

The formation of a liquid phase during the compression of a pure gas depends on the thermodynamic behavior of the gas.⁵² Two types of behavior are illustrated in Fig. 5-48a and b on temperature-entropy diagrams. The behavior shown by Fig. 5-48a is for isentropic compression from a to b , and compression results in increased superheat with no tendency for condensation to occur. If the compressed gas were intercooled to the original temperature, it would be completely liquefied. Intercooling may be carried to a somewhat higher temperature, avoiding the saturation curve. A second stage of compression following the intercooler will not result in liquefaction. If the initial pressure and temperature are well away from the saturation curve and into the superheat region, no condensation will occur on intercooling to the initial temperature. The behavior in Fig. 5-48a is characteristic of most pure gases including the hydrocarbon gases through propane.

Butane and higher-molecular-weight hydrocarbons have the type of T - S diagram shown in Fig. 5-48b. With these gases, isentropic compression of the saturated vapor may result in condensation. This is shown by the path a to b in this diagram, which crosses the saturation curve into the liquid region.

The behavior of gas mixtures is described in Chap. 8. The formation of condensate in intercoolers handling gas mixtures is frequently encountered. Provision to remove the condensate before returning the gas to

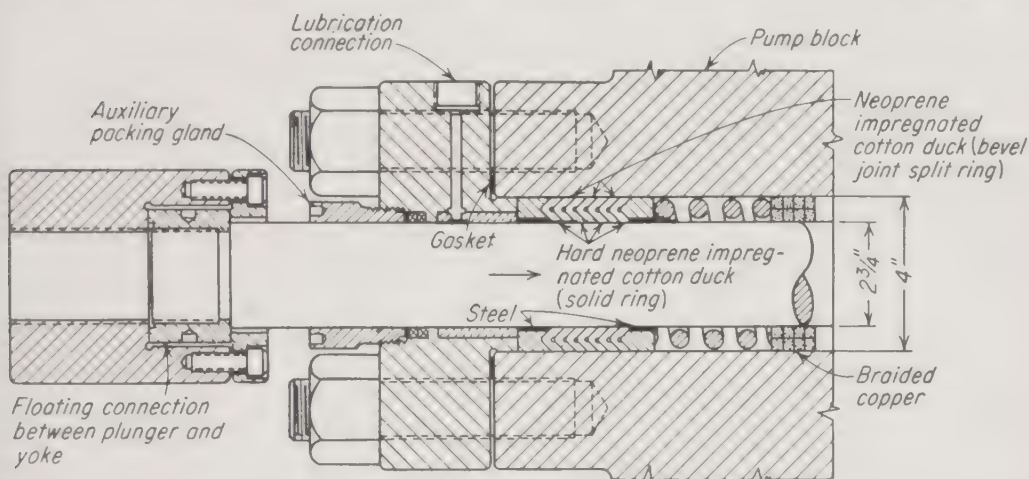


FIG. 5-49. Coal-oil paste pumps. [From C. C. Chaffee and L. L. Hirst, *Ind. Eng. Chem.*, **45**:822 (1953), U.S. Bureau of Mines.]

subsequent stages must be made, since the presence of incompressible liquid may crack the cylinders or cause other serious damage to the machine and injury to personnel. Condensation may sometimes be avoided by eliminating the intercoolers or controlling the temperature of the cooling water.

Multiple-stage compressors with intercoolers have reduced power requirements because the compression approaches isothermal rather than adiabatic operation. However, the difference in power requirements between isothermal and adiabatic operation becomes less as the heat capacity of the gas increases. For this reason, the saving in power by using intercoolers is not so great with the higher-molecular-weight gases which condense at relatively lower temperatures.

Liquid Pumps. The pumps used to deliver liquids under high pressures are usually of the single-acting type, operating either vertically or horizontally. A cross section through the packing assembly of those used by the Bureau of Mines⁵⁷ to handle coal-oil paste is shown in Fig. 5-49. These are slow-speed units and are steam-driven to obtain variable output.

For small-capacity operations, plunger-type pumps operated by hand

⁵⁷ C. C. Chaffee and L. L. Hirst, *Ind. Eng. Chem.*, **45**:822 (1953).

are suitable for use to 30,000 psi. Motor-driven units are available for use up to 50,000 psi. Oil raised to high pressure by these pumps may be

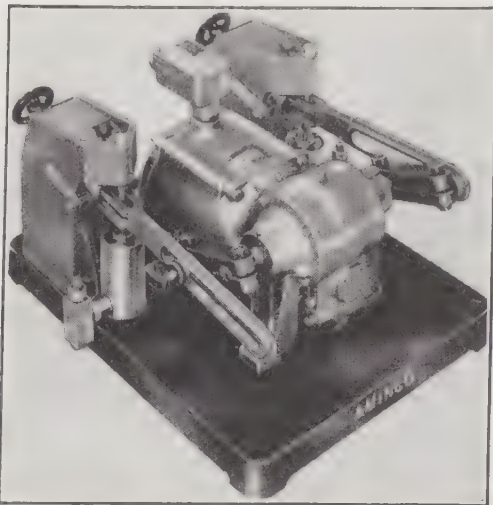


FIG. 5-50. Micro-Flex Pump for pressures up to 30,000 psi. (*American Instrument Company, Inc.*)

used to operate a hydraulic intensifier or a mercury gas compressor. It may also be used to compress gas in a cylinder when the solubility of the gas in the oil is not detrimental.

Two types of small high-pressure pumps are shown in Figs. 5-50 and 5-51. These are available for pressures up to 50,000 psi and for capacities from $\frac{1}{8}$ to many gallons per hour. The discharge rate is subject to precise adjustment through control of the length of stroke while the pump is in operation. An arrangement of double-ball check valves is used.⁵⁸ The design used

in the pump in Fig. 5-51 is shown in Fig. 5-52. With double-ball check valves on suction and discharge there is a second valve to function in the event that a foreign particle should

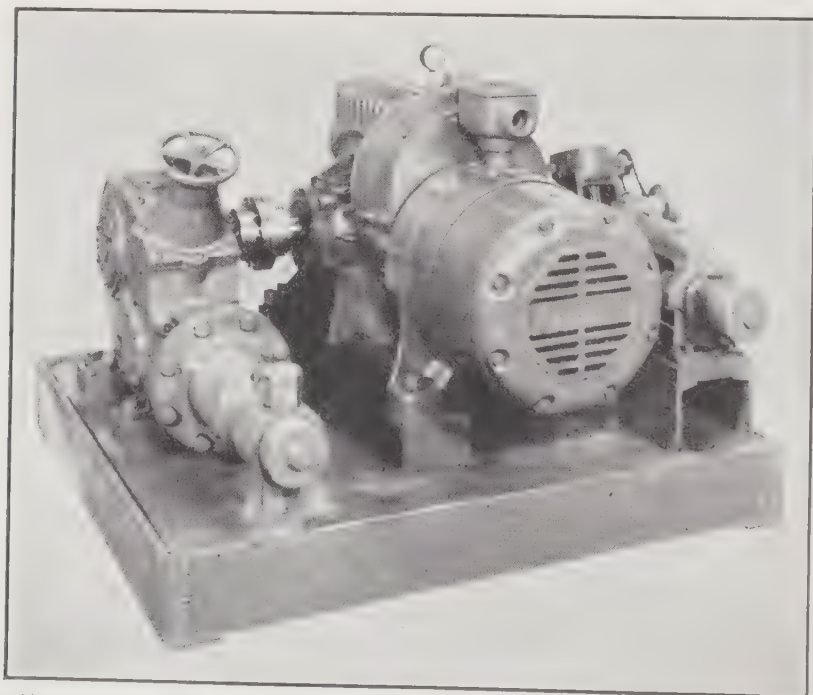


FIG. 5-51. Controlled-volume pump for continuous operation up to 50,000 psi. (*Milton Roy Company.*)

⁵⁸ *Milton Roy Company Bull. 555*, Philadelphia, Pa., 1955.

lodge under one check valve. This avoids the possibility of erratic pumping or loss of pressure. Above 25,000 psi, AISI 4340 steel is used for the body and tungsten carbide alloy for the balls, seats, and plungers. The plunger is free to float in the crosshead to minimize misalignment and wear. A special unsupported-area type of packing is used for the plunger as shown at *b*. It consists of alternating male and female rings of hard and soft

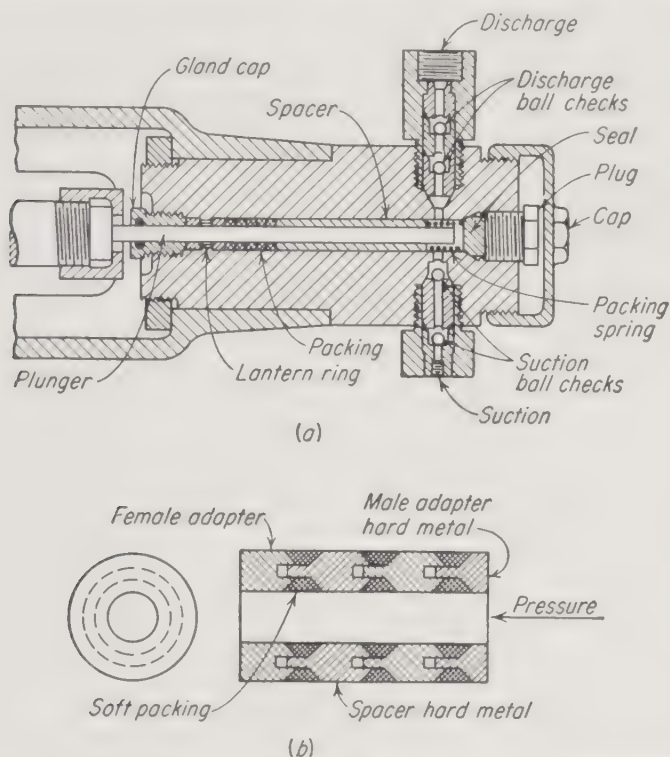


FIG. 5-52. Liquid end of controlled-volume pump showing (a) valves and (b) plunger packing. (Milton Roy Company.)

metal. The area across the male or pressure end of each ring is greater than across the soft ring. The soft rings are thus under greater pressure than the fluid and are forced out from between the hard rings and against the plunger and side walls, thus effecting the seal. The packing automatically compensates for wear. A spring acts on a spacer to hold the packing in place and maintain alignment. It does not provide any force to produce the seal. Since there is little change in specific volume of the liquid, clearance between the piston and cylinder walls does not affect the capacity of the pump as it would with a more compressible fluid. The loose-fitting plunger forces the fluid out of the cylinder by displacement. The delivery rate is not constant but fluctuates from a maximum to zero at each stroke.

The Hills-McCannameter⁵⁹ employs a bellows to provide packless con-

⁵⁹ Hills-McCanna Company, Bulletin AP-54, Chicago, Ill., 1954.

TABLE 5-2. CLOSURES FOR HIGH-PRESSURE VESSELS†

Closure type	Fig. no.	Time for opening	Pressure range, psi	ID range, in.	Temperature range limiter	Ease of fabrication	Space for head connections	Remarks
Solid end bored.....	5-14a	Permanent	Unlimited	Up to 6-8	Metal	Simple	Unobstructed end area	Suitable for solid-alloy or lined construction
Solid end, forged or cast.....	5-14b	Permanent	Unlimited	6-72	Metal	Equipment costly	Unobstructed end area	Solid or electroplated liners
Flat disk, welded.....	5-14c	Permanent	To 1,000 or 2,000	To 6	For lower temperatures	Simple	Limited end area	Solid or sheet-metal liner
Formed cup, butt-welded.....	5-14d	Permanent	10,000-15,000	Unlimited, but wall thickness limited to 6 in.	Weld metal	Simple	Depends on design	Solid only in smaller sizes
Screwed plug, welded.....	5-14e	Permanent	15,000-20,000	6 in., length limited to lathe length	For lower temperatures	Simple	Limited end area	Not good design for absorbing overpressures, solid or fabricated liners
Bolted flange, welded.....	5-15a	Long	Up to 6,000	To 24 at max. pressures	Bolt metal	Simple with standard flanges	Full end area	Suitable for sheet-metal lining
Bolted flange, screwed.....	5-15b	Long	Up to 6,000	To 12	Moderate range	Simple	End area unobstructed	Suited to sheet-metal linings and composite metal
Ipaticoff closure.....	5-15c	Long	To 6,000	To 6	Gasket material, high-temperature service	Costly; forgings and lathe work	Smaller end area than other flanges	Never sticks, easy to clean, requires frequent gasket removal, solid construction only
Flange neck, welded.....	5-15d	Long	To 10,000	Over 5 for best advantage	Weld metal unless forged	Simple	Opening and end area seriously reduced	Not suitable for liners in small sizes
Vickers-Anderson joint.....	5-15e	Quick opening	To 25,000	Over 12 for large openings	Gasket, advantageous for high temperature using self-sealing gasket	Critical machining difficult	Full end area	Light weight, economical of solid alloys, linings also practical

Screw plug, gasketed.....	5-16a	Quick opening	To 50,000, heat-treated steels satisfactory	Up to 2	Gasket, for high-temperature application	Simple, low cost	End area available	Uses can-type liner only at high pressures, not for frequent opening and closing
Screw sleeve and plug.	5-16b	Quick opening—requires heavy wrench if over 1 in. in diameter	To 5,000	Up to 3	Gasket, self-sealing gasket desirable	Careful machine work required	Limited end area	Satisfactory for high temperatures with corrosion-resistant linings
Compression head.....	5-16c	Quick opening	To 100,000 if self-sealing gasket is used	1-6	Cap-screw material	More critical than with flanges	Limited end area	Adapted to any type of corrosion-proof construction
Tapered cap-ring closure	5-16d	Quick opening	To 50,000 if self-sealing gasket is used	6-16	Stress in bolts	Design critical, fabrication less so	Limited end area	Light weight, difficult to clean, economical for solid-alloy construction, sheet-metal linings used
O-ring closure.....	5-16e	Quick opening	To 30,000	Up to 3	Gasket material	Relatively simple	Limited end area	Gasket easily replaced
Bridgman head.....	5-17a	Not easy to open	100,000 30,000 15,000	Up to 1 Up to 3 Up to 12	Previous heat-treatment of steel	Requires precision in manufacture	Limited end area	Careful cleaning and inspection required after each opening
Modified Bridgman closure.....	5-17c	Quick opening	Unlimited, self-sealing	3-18	Teflon gasket	Requires precision in manufacture	Ends restricted, high radial stress	Not easy to clean, solid construction or can-type liners
Flanged Bridgman closure.....	5-17b	Long	Up to 25,000	8-72	Bolt material	Requires care and experience	Ample end area	Sheet-metal linings and also multilayer construction satisfactory
Bolted flange, Δ ring.....	5-13d	Long	Up to 50,000, probably higher self-sealing	2-36	Metals	Relatively simple	Full end area	Popular large-vessel closure in U.S.

† From D. Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**:769 (1943).

struction in a positive-displacement design for pressures up to 10,000 psi and flow rates from 5 ml/hr to 6 gal/hr.

A pump with a novel mechanical drive has been devised so that the discharge from one cylinder increases as that from another decreases. The result is a duplex pump with a constant discharge rate.⁶⁰

An interesting variation of the plunger pump permits hot oil or corrosive slurries to be pumped without introducing them into the body of the pump. An external reservoir is placed in the line between the pump cylinder and the valves. Thus, oil at moderate temperatures oscillates back and forth between the pump cylinder and one end of the reservoir, sucking the hot oil into the other end and forcing it out through the valves. When this arrangement is used to pump a slurry, a small amount of fluid free from solids is continually introduced by an auxiliary pump between the pump cylinder and the reservoir to flush the slurry from the pump end of the system. Such an arrangement for pumping an 18- to 100-mesh aluminum chloride-hydrocarbon mixture to a reactor under 700 to 800 psi is shown in Fig. 7-32.

For pressures above 25,000 to 50,000 psi, pressure intensifiers are used. These have been described under compressors, although at such high pressures the distinction between a pump and a compressor loses its significance.

The Sprague Engineering Corporation's high-pressure pump uses compressed air up to 150 psi to operate a large piston. Directly connected to the large piston is a small piston which pumps oil or water at pressures up to 30,000 psi. The unit pumps continuously or will hold a definite high pressure when the air is set at a definite low pressure.

NOMENCLATURE

- A* Cross-sectional area of piston, sq in.
- a* Cross-sectional area of annular space between cylinder and piston, sq in.; also a constant
- C* Gauge constant, lb force/(sq in.)(lb mass)
- C_p* Heat capacity at constant pressure, Btu/(lb mole)(°F)
- d* Diameter of Δ ring, in.
- E* Modulus of elasticity $\sigma = E\epsilon$ (see Chap. 6)
- f* Coefficient of friction between Δ ring and cavity
- g* Local acceleration due to gravity, ft/sec²
- g_c* Conversion factor, 32.1740 (lb mass)(ft)/(lb force)(sec²)
- H* Enthalpy, Btu/lb mole
- K* r_2/r_1
- k* Coefficient of compressibility
- L* Axial length of Δ ring, in.

⁶⁰ Milton Roy Company.

M	Molecular weight
p	Absolute pressure, psi
p_a	Atmospheric pressure, psi
p_c	Critical pressure, psi
p_R	Reduced pressure, p/p_c
p_1	Pressure before compression; also gauge pressure on inner wall of a cylinder, psi
p_2	Pressure after compression; also gauge pressure on outer wall of a cylinder, psi
R	Gas-law constant
r	Radial distance from the axis to a point in a cylinder; r_1 is inside radius, r_2 is outside radius of solid wall
S	Entropy, Btu/(lb mole)(°R)
ΔS_i	Entropy change for an ideal gas from T_1 to T_2
T	Absolute temperature, °K or °R
T_c	Critical temperature, °R
T_1	Absolute temperature before compression, °K or °R
T_2	Absolute temperature after compression, °K or °R
T_R	Reduced temperature T/T_c
t	Temperature, °F or °C; also thickness of cylinder wall
v	Volume of 1 lb mole of gas; v_1 before compression, cu ft
W	Mass of weights on dead-weight piston, lb
W_c	Theoretical work of compression, ft-lb/lb mole
w	Mass of piston itself, lb
x	Δ -gasket dimension (see Fig. 5-13d)
z	Compressibility factor pv/RT
γ	Ratio of heat capacity at constant pressure to heat capacity at constant volume, C_p/C_v
δ_B	Decrease in radius of piston
δ_A	Increase in internal radius of cylinder
ν	Poisson's ratio
Φ	$R \left[z + T \left(\frac{\partial z}{\partial T} \right)_p \right]$

CHAPTER 6

THICK-WALLED CYLINDERS

The majority of pressure vessels are cylindrical. When a vessel is designed to withstand a low to moderate internal pressure, the wall thickness is not great and the tensile stress is almost uniformly distributed through the wall from its inner to its outer surface. Under these conditions, the relation between the stress in the cylinder wall and the internal pressure p_1 is

$$\sigma_t = \frac{p_1 r_1}{t} \quad (6-1)$$

For a given internal radius r_1 and a tensile stress in the wall at the elastic limit, the pressure may be increased if the wall thickness is increased proportionately. As the wall thickness is increased to withstand higher internal pressures, the distribution of tensile stress throughout the wall becomes nonuniform and the wall thickness must be increased more than in proportion to the pressure. The calculation of the stresses and strains in a thick-walled cylinder must allow for the nonuniform distribution of stresses throughout the wall and to do this a more complicated analysis is required.

When thick cylinder walls deform elastically and are not stressed beyond the range of elastic behavior, the formulas of Lamé may be used to calculate the distribution of stresses. These will be derived in the following text. It will be evident from these formulas that a thick-walled cylinder subjected to internal pressure only is more highly stressed near its inner surface than near its outer surface. Thus the inner layers may be stressed to near or beyond the elastic limit, while the outer layers are under relatively low stress. A limit set at the pressure which produces inelastic strains at the inner wall is unnecessarily low and does not make effective use of the strength of the steel.

More effective use of the strength of the steel can be made in several ways. The wall may be constructed in layers prestressed by the proper amount, so that the initial residual stress must be overcome and reversed by the application of internal pressure. This type of construction permits the design of a vessel having the stresses uniformly distributed throughout a thick wall when the vessel is subjected to a specified pres-

sure.) Under these circumstances and at this one pressure, the thin-wall formula [Eq. (6-1)] again applies. The wall may be constructed of layers of wire, tape, sheets, or of several concentric cylinders. Initial residual stresses may be set up in solid-walled cylinders. These arise from temperature gradients associated with heat-treating, or they may come from previously subjecting the cylinder to pressures which produce stresses above the elastic limit. When the latter pressure is released, the part of the cylinder nearer the bore is in residual compression. The cylinder will then behave elastically when subjected to pressures up to the prestressing pressure. This prestressing treatment is known as autofrettage. The Lamé¹ equations apply only to those regions subjected to elastic deformation. In order to know when these equations do not apply, a criterion for the limits of elastic action is required. Several such criteria have been proposed, but only a few of these have been shown to be valid in the circumstances of interest here. These will be discussed. The limit to the range of elastic action defines the range of application of the Lamé equations, but it does not indicate the limiting internal pressure which a thick-walled cylinder will withstand without bursting.

As the pressure in a thick-walled cylinder is increased, inelastic deformation occurs first at the inner surface. Then it progresses through the wall as the internal pressure is increased until the outer surface finally deforms inelastically. The entire cylinder is then in a plastic condition. In certain cases, a pressure increase of the order of twofold is required to cause the inelastic deformation to progress from the inner to the outer surface. A considerable portion of the strength of a thick-walled cylinder is in the range of inelastic action, and the distribution of stresses and strains under these conditions is important. Equations for this range will be developed after elastic behavior is considered.

Bursting occurs at a pressure above that where the entire cylinder is in a plastic condition.

6-1. Elastic Behavior. Stresses in the Walls. Consider a thick-walled cylinder, long relative to its diameter and closed at both ends. At some distance from either end, visualize cutting out a slice of unit length from the cylinder. Half this slice is shown in Fig. 6-1. This half slice may be further divided into thin annuli of differential thickness. Consider now a static-force balance on one of these half annuli formed when

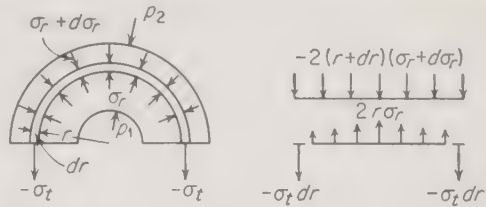


FIG. 6-1. Force balance on section of thick-walled cylinder.

¹ G. Lamé and B. P. E. Clapeyron, *Mémoire sur l'équilibre intérieur des corps solides homogènes*, *Mémoires présentés par divers savans*, vol. 4, 1833.

the annulus is cut by a diametral plane containing the axis of the cylinder. The forces may be resolved into radial forces acting on the inner surface, radial forces acting on the outer surface, circumferential forces acting on the edge of the half annulus, and longitudinal forces acting on the ends of the slice. The circumferential forces are due to circumferential stresses in the steel, and these must be balanced by the net components of the radial forces acting in the opposite direction. The circumferential force is $2\sigma_t dr$. The component of the radial forces acting on the inner surface is $2r\sigma_r$, and that on the outer surface is $2(r + dr)(\sigma_r + d\sigma_r)$. Equating these forces gives

$$2r\sigma_r - 2(r + dr)(\sigma_r + d\sigma_r) = -2\sigma_t dr$$

Expanding, and neglecting the second-order differential $dr d\sigma_r$, this reduces to

$$-\sigma_t + \sigma_r + r \frac{d\sigma_r}{dr} = 0 \quad (6-2)$$

The longitudinal stresses balance one another, but the longitudinal strain is the result of stresses in three directions. The strain due to σ_z is σ_z/E , that due to σ_t is $\nu\sigma_t/E$, and that due to σ_r is $\nu\sigma_r/E$; or the total longitudinal strain ϵ_z is

$$\epsilon_z = \frac{\sigma_z}{E} - \frac{\nu\sigma_r}{E} - \frac{\nu\sigma_t}{E} \quad (6-3)$$

It is reasonable to assume that ϵ_z and σ_z are constant throughout the wall if the wall is not distorted from its original cylindrical shape; then

$$\sigma_t + \sigma_r = \frac{\sigma_z}{\nu} - \frac{E\epsilon_z}{\nu} = 2a \quad (6-4)$$

where a is a constant. Substituting in Eq. (6-2),

$$-2a + 2\sigma_r + r \frac{d\sigma_r}{dr} = 0 \quad (6-5)$$

This can be integrated to give

$$\sigma_t = \frac{p_1 - p_2 K^2 + (r_2^2/r^2)(p_1 - p_2)}{K^2 - 1} \quad (6-6)$$

$$\sigma_r = - \frac{p_2 K^2 - p_1 + (r_2^2/r^2)(p_1 - p_2)}{K^2 - 1} \quad (6-7)$$

where p_1 = internal pressure at r_1

p_2 = external pressure at r_2

$K = r_2/r_1$

Then dividing by p_1 ,

$$\frac{\sigma_t}{p_1} = \frac{1 - (p_2/p_1)K^2 + (r_2^2/r^2)(1 - p_2/p_1)}{K^2 - 1} \quad (6-8)$$

and

$$\frac{\sigma_r}{p_1} = - \frac{(p_2/p_1)K^2 - 1 + (r_2^2/r^2)(1 - p_2/p_1)}{K^2 - 1} \quad (6-9)$$

When p_2 is zero or negligible, the maximum stress is a circumferential tensile stress and occurs at the inner radius r_1 . At this position

$$\frac{(\sigma_t)_{r_1}}{p_1} = \frac{K^2 + 1}{K^2 - 1} \quad (6-10)$$

and

$$\frac{(\sigma_r)_{r_1}}{p_1} = 1 \quad (6-11)$$

For a cylinder closed at the ends, the longitudinal stress will result from the force due to the pressure on the ends $p_1\pi r_1^2$. This force is uniformly distributed over the cross-sectional area of the walls $\pi(r_2^2 - r_1^2)$, and the longitudinal stress is

$$\sigma_z = \frac{p_1}{K^2 - 1} \quad (6-12)$$

The distribution of stresses, expressed as ratios of σ_t and σ_r to the yield strength σ_y , through a solid wall with $K = 2$ when undergoing only elastic strains with an external pressure of zero is shown in Fig. 6-2. Both circumferential and radial stresses are largest at the inner surface, and the maximum stress is σ_t at r_1 . All stresses are arbitrarily designated as positive when in tension and negative in compression. The radial stresses will ordinarily be in compression and are negative.

The circumferential and radial stress at any point in the wall, due to either internal pressure alone or external pressure alone, may be calculated from Eqs. (6-6) and (6-7). When p_2 is zero, Eq. (6-6) becomes

$$(\sigma_t)_{p_1} = \frac{p_1(1 + r_2^2/r^2)}{K^2 - 1} \quad (6-13)$$

and when p_1 is zero, Eq. (6-6) becomes

$$(\sigma_t)_{p_2} = - \frac{p_2(K^2 + r_2^2/r^2)}{K^2 - 1} \quad (6-14)$$

If these are added, they give the total stress at a point when p_1 and p_2

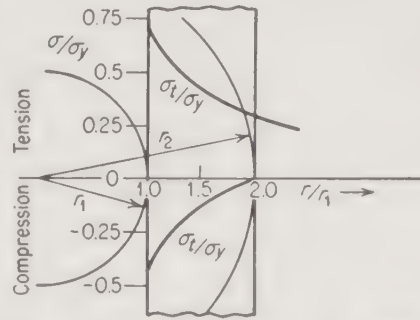


FIG. 6-2. Distribution of stress through cylinder wall with $K = 2$, $p_2 = 0$.

are both acting together; thus $\sigma_t = (\sigma_t)_{p_1} + (\sigma_t)_{p_2}$. This demonstrates the additive property of elastic stresses. The stress caused by an internal pressure acting alone may be added to that caused by an external pressure acting alone, and the sum gives the stress at the same point when both pressures are acting simultaneously. This additive property can be applied to annular sections of a cylinder, and then the radial stresses acting on the inner and outer surfaces of the annulus are entirely comparable to inner and outer pressures.

Elastic Strains. The elastic strains in a cylindrical wall in the radial, circumferential, and longitudinal directions are each influenced by the stresses in all three directions and are given by

$$\epsilon_r = \frac{1}{E} (\sigma_r - \nu\sigma_t - \nu\sigma_z) \quad (6-15)$$

$$\epsilon_t = \frac{1}{E} (\sigma_t - \nu\sigma_r - \nu\sigma_z) \quad (6-16)$$

$$\epsilon_z = \frac{1}{E} (\sigma_z - \nu\sigma_t - \nu\sigma_r) \quad (6-17)$$

These equations may be expressed in terms of the internal and external pressures and the dimensions of the cylinder. A convenient ratio is that of the elastic strain at any radius r to the strain when under simple tension equal to the internal pressure. This latter ratio is shown on the left in the following equations,

$$\frac{\epsilon_r E}{p_1} = - \frac{2\nu - 1 + (1 - \nu)K^2 \frac{p_2}{p_1} + (1 + \nu) \left(1 - \frac{p_2}{p_1}\right) \frac{r_2^2}{r^2}}{K^2 - 1} \quad (6-18)$$

$$\frac{\epsilon_t E}{p_1} = \frac{1 - 2\nu + (\nu - 1) \frac{p_2}{p_1} K^2 + (1 + \nu) \left(1 - \frac{p_2}{p_1}\right) \frac{r_2^2}{r^2}}{K^2 - 1} \quad (6-19)$$

$$\frac{\epsilon_z E}{p_1} = \frac{1 - 2\nu + 2\nu K^2 \frac{p_2}{p_1}}{K^2 - 1} \quad (6-20)$$

For $p_2 = 0$ and at $r = r_1$,

$$\frac{(\epsilon_r)_{r_1} E}{p_1} = - \left[\frac{(K^2 + 2)\nu}{K^2 - 1} + 1 \right] \quad (6-21)$$

$$\frac{(\epsilon_t)_{r_1} E}{p_1} = \frac{K^2 + 1}{K^2 - 1} + \nu \quad (6-22)$$

$$\frac{(\epsilon_z)_{r_1} E}{p_1} = \frac{1 - 2\nu}{K^2 - 1} \quad (6-23)$$

The displacement of a point on the inner surface in the radial direction is denoted by δ_1 and is related to the circumferential strain at r_1 .

$$\delta_1 = \frac{2\pi r_1(\epsilon_t)_{r_1}}{2\pi} = r_1(\epsilon_t)_{r_1} \quad (6-24)$$

Multilayer Walls—Wire and Tape Winding. A thick wall may be built up in such a manner that the circumferential stress is distributed uniformly throughout the thickness when the cylinder is subjected to a specified internal pressure. This is done by building up the wall, layer upon layer, each under a predetermined tensile stress σ_w which varies from the inner surface to the outer.

As more layers are added, the outer layers act on the inner in the same manner as an external pressure. When the wall is completely fabricated and before internal pressure is applied, the inner layers are under compression and the outer are under tension. As internal pressure is applied, the compression in the inner layers is at first relieved, and these layers are then put under tension as the internal pressure is increased. At the specified internal pressure, the tension in each layer is the same throughout the wall.

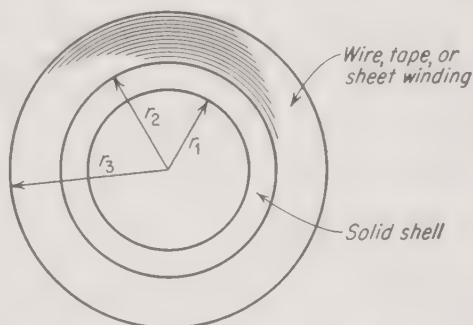


FIG. 6-3. Cylinder with outer wound layers.

A method of calculating the stresses in a multilayer wall will be described for three cases. Consider a cylinder such as shown in Fig. 6-3 composed of a solid-steel wall from its inner radius r_1 to a radius r_2 and of thin layers of sheet, ribbon, or wire from r_2 to an outer radius r_3 . Let $r_2/r_1 = K_1$ and $r_3/r_1 = K_2$. When the cylinder is being constructed, it will normally be empty, and the internal-fluid pressure p_1 acting at r_1 is zero. Similarly, there will be no longitudinal stress resulting from the internal-fluid pressure acting on the end closures. The layers may be wound onto the inner solid cylinder under a tension which varies as each layer is added, or this tension may be constant during the winding.

Variable Tension in the Wire. CASE 1. In this instance the tension in the wire will be varied during its application. The tension or stress σ'_t is to be constant throughout the wound layer when the cylinder has been completed and is under a fixed internal-fluid pressure p'_1 . Comstock² describes this case. The external-fluid pressure at r_3 is zero. Under these conditions, the tension in the winding will act as a pressure p'_2 on the inner cylinder at r_2 , and this together with the internal pressure

² C. W. Comstock, *Trans. Am. Inst. Chem. Engrs.*, **39**:299 (1943).

p'_1 gives the following circumferential-stress distribution in the inner cylinder

$$\sigma_t = p'_1 \frac{1 - (p'_2/p'_1)K_1^2 + (r_2^2/r^2)(1 - p'_2/p'_1)}{K_1^2 - 1} \quad (6-25)$$

where $p'_2 = \sigma'_t(K_2 - K_1)/K_1$ (6-26)

Substituting Eq. (6-26) into (Eq. (6-25) and for $r_2 > r > r_1$,

$$\sigma_t = p'_1 \frac{1 + \sigma'_t \frac{K_1^2}{p'_1} - \frac{\sigma'_t}{p'_1} K_1 K_2 + \frac{r_2^2}{r^2} \left(1 + \frac{\sigma'_t}{p'_1} - \frac{\sigma'_t K_2}{p'_1 K_1} \right)}{K_1^2 - 1} \quad (6-27)$$

The greatest value of σ_t from Eq. (6-27) is at r_1 , where

$$(\sigma_t)_{r_1} = p'_1 \frac{K_1^2 + 1 - (2\sigma'_t K_1/p'_1)(K_2 - K_1)}{K_1^2 - 1} \quad (6-28)$$

For a fixed value of $(\sigma_t)_{r_1}$, such as the allowable working stress σ_{ta} , Eq. (6-28) may be used to determine the constant stress σ'_t in the winding under the specified internal pressure.

When the cylinder is not subjected to internal pressure, the inner wall is under compression. This compressive stress may be found by subtracting the stress due to the internal pressure from that given by Eq. (6-28), and it is properly the allowable stress σ_{tc} , where

$$-\sigma_{tc} = \sigma_{ta} - p'_1 \frac{K_2^2 + 1}{K_2^2 - 1} \quad (6-29)$$

The proportions of the cylinder are given by K_1 and K_2 . These proportions and the winding tension σ_w are determined by the specification of the stress σ_{ta} (at the temperature of operation), the stress $-\sigma_{tc}$ (at the temperature of fabrication), the internal-fluid pressure p'_1 , and the tension in the wire when the cylinder is at this pressure σ'_t .

From Eq. (6-29)

$$K_2^2 = \frac{\sigma_{ta} + \sigma_{tc} + p'_1}{\sigma_{ta} + \sigma_{tc} - p'_1} \quad (6-30a)$$

and, with $(\sigma_t)_{r_1} = \sigma_{ta}$ in Eq. (6-28),

$$K_1^2 = \frac{\sigma_{ta} - 2\sigma'_t K_2 + p'_1}{\sigma_{ta} - 2\sigma_t - p'_1} \quad (6-30b)$$

Equations (6-25) to (6-28) refer only to the stress σ_t when the complete cylinder is under the internal pressure p'_1 . For other values of the internal pressure p_1 , the stress in the wound layers will not be uniform. The stresses in the cylinder wall may then be calculated by considering the stresses at any radius due to the separate effects of (a) the winding

and internal pressure p'_1 , and (b) the internal pressure p_1 . The stress with various values of p_1 is obtained by correcting for the difference between (a) and (b). This is done as follows. When the internal pressure is p_1 , the stress σ_t in the winding at any radius is obtained by correcting σ'_t for the stress due to the difference in pressure $(p'_1 - p_1)$ acting on the whole cylinder considered as a unit. The latter stress correction is obtained from Eq. (6-6) as

$$\sigma_{t, \text{corr}} = \frac{(p'_1 - p_1)(1 + r_3^2/r^2)}{K_2^2 - 1} \quad (6-31)$$

Thus with an internal pressure p_1 , the stress distribution in the inner solid cylinder may be obtained by subtracting Eq. (6-31) from Eq. (6-27), and the stress distribution in the outer wound layer may be obtained by subtracting Eq. (6-31) from the constant stress σ'_t . When $p_1 = 0$, this procedure will give the stresses in the cylinder due to the tension in the windings alone with the outer layers complete.

Wire Tension Determined by Integration. The tension σ_w of each layer as it is wound on the cylinder will differ from its tension in the completed cylinder. To find the tension σ_w at radius r , the tension (or compression) produced by the layers from r to r_3 is subtracted from the tension at radius r in the completed cylinder as follows. The stresses σ_t and σ_r in the winding at zero internal pressure for $r_3 > r > r_2$ are given by

$$\sigma_t = \sigma'_t - \frac{p'_1(1 + r_3^2/r^2)}{K_2^2 - 1} \quad (6-32)$$

Figure 6-4 shows a balance of forces in the direction indicated by the arrow marked r over the left-hand quarter of the outer cylinder from r to r_3 . The components of the radial stresses acting in this direction on the boundary at r are balanced by the sum of the circumferential stresses acting on thin annuli of this outer cylinder, each of thickness dr . This sum is represented by $\int_r^{r_3} \sigma_t dr$, and the balance is

$$\sigma_r r = - \int_r^{r_3} \sigma_t dr = \left(-\sigma'_t + \frac{p'_1}{K_2^2 - 1} \right) \int_r^{r_3} dr + \frac{p'_1 r_3^2}{K_2^2 - 1} \int_r^{r_3} \frac{dr}{r^2} \quad (6-33)$$

after integrating,

$$-\sigma_r = \left(\frac{r_3}{r} - 1 \right) \left[\sigma'_t - \frac{p'_1}{K_2^2 - 1} \left(\frac{r_3}{r} + 1 \right) \right] \quad (6-34)$$

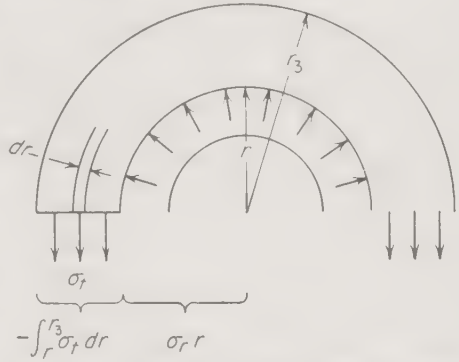


FIG. 6-4. Force balance over outer cylinder from r to r_3 .

The circumferential stress σ_{t_0} at r due to the outside layers from r_3 to r is obtained from Eq. (6-6) by considering the wall from r_1 to r to be subjected to the pressure σ_r on the outer boundary at r . Then

$$\sigma_{t_0} = -\sigma_r \frac{r^2 + r_1^2}{r^2 - r_1^2} \quad (6-35)$$

and the winding tension σ_w is $\sigma_t - \sigma_{t_0}$. Making the appropriate substitutions from Eqs. (6-32), (6-34), and (6-35),

$$\sigma_w = \sigma_t'' \frac{r_3(r^2 + r_1^2) - 2rr_1^2}{r(r^2 - r_1^2)} - \frac{2p_1' r_1^2}{r^2 - r_1^2} \quad (6-36)$$

An example is given by Comstock to show the range of stresses in the

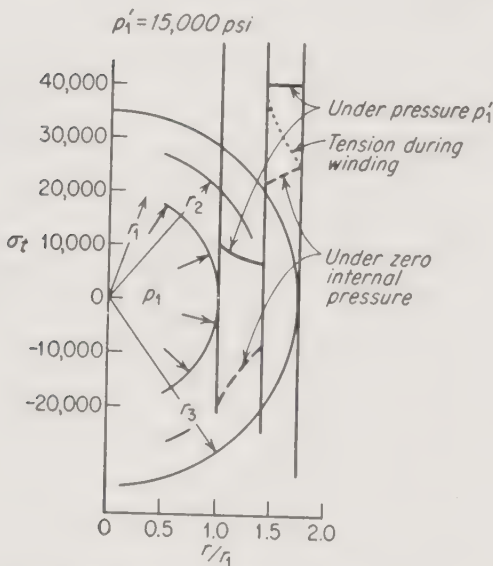


FIG. 6-5. Stress distribution in layer-wound cylinder.

stress for seven different values of the ratio $r/r_1 = K$. These stresses are shown in Fig. 6-5. When the winding is completed, but before the internal pressure is applied, the inner walls of the vessel are under compression and the winding is under tension. As internal pressure is applied, the compression is relieved, and then the entire wall is subjected to tension which is uniformly distributed through the winding at the specified internal pressure. The uniform stress distribution uses the strength of the steel effectively.

Layer Tension by Summation. CASE 2. The case of a cylinder wall constructed throughout of n prestressed laminations of a uniform finite thickness h is developed by Seely and Smith.³ These authors give a

³ F. B. Seely and J. O. Smith, "Advanced Mechanics of Materials," 2d ed., John Wiley & Sons, Inc., New York, 1952.

cylinder at several radii during the winding operation and also in the completed cylinder: the specified internal pressure p_1' is 15,000 psi. The allowable tensile stress at inside of tube σ_{t_a} is 10,000 psi, and the allowable compressive stress at inside of tube $-\sigma_{t_c}$ is 20,000 psi. Tension in the wire under full load σ_t'' is 40,000 psi. From Eq. (6-30), $K_2 = 1.732$; $K_1 = 1.422$.

The tension in the completed coil for $p_1 = 0$ may be computed for any value of K between K_1 and K_2 by using Eq. (6-32), and the tension under which the wire must be applied will be found by Eq. (6-36). Table 6-1 shows the circumferential

method for calculating the wrapping tension σ_w in each layer. The radii to the outer surface of layers 1, 2, . . . , n , respectively, are defined as r_1, r_2, \dots, r_n ; x_1, x_2, \dots, x_n are the radii to the mid-thickness of each layer; and p_1, p_2, \dots, p_{n-1} are the wrapping pressure or external pressure on each layer due to the next single layer as it is applied. The stress in any layer is obtained by adding the stresses caused by the internal pressure to the sum of all the wrapping pressures, from that caused by the outer layer down to and including that caused by the layer

TABLE 6-1

K	Tension of application σ_w , psi	Tension in completed coil with no internal pressure, psi
1.422	36,446	21,370
1.450	34,689	21,798
1.500	32,084	22,500
1.550	30,002	23,135
1.600	28,301	23,712
1.650	26,854	24,249
1.732	25,000	25,000

under consideration. The circumferential stress in any layer m when the cylinder is complete and subjected to the specified internal pressure p_1' is nearly constant at the stress σ_t'' and is

$$\sigma_{t_m} = \sigma_t'' = p_1' \frac{r_0^2(r_n^2 + x_m^2)}{x_m^2(r_n^2 - r_0^2)} + \frac{p_{m-1}r_{m-1}}{h} - \left(1 + \frac{r_0^2}{x_m^2}\right) \sum_{m=m}^{n-1} \frac{p_m r_m^2}{r_m^2 - r_0^2} \quad (6-37)$$

By starting with the outer layer where p_m is zero, this equation may be applied successively to each layer, and the wrapping pressure p_{m-1} is obtained. In this way, there is only one unknown wrapping pressure to be evaluated at each step. The corresponding wrapping tension σ_w is found from Eq. (6-1) to be

$$\sigma_{w_m} = \frac{p_{m-1}r_{m-1}}{h}$$

Wire Applied under Constant Tension. CASE 3. Here the wire is applied at a constant tension σ_w during the winding operation. Newitt⁴ gives the stress distribution. The stress σ_t in the tangential direction, at

⁴ D. M. Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.

any radius r , in the completed winding due alone to the compression by the layers from r to r_3 is

$$\sigma_r \frac{r^2 + r_1^2}{r^2 - r_1^2}$$

The circumferential stress in the completed coil at this radius is then

$$\sigma_t = \sigma_w + \sigma_r \frac{r^2 + r_1^2}{r^2 - r_1^2} \quad (6-38)$$

From Eqs. (6-2) and (6-38)

$$\sigma_r + r \frac{d\sigma_r}{dr} = \sigma_t = \sigma_r \frac{r^2 + r_1^2}{r^2 - r_1^2} + \sigma_w \quad (6-39)$$

This may be rearranged and integrated and the constant of integration evaluated for $\sigma_r = 0$ at $r = r_3$. The resulting equation is

$$\sigma_r = - \frac{r^2 - r_1^2}{2r^2} \sigma_w \ln \frac{r_3^2 - r_1^2}{r^2 - r_1^2} \quad (6-40)$$

and from Eq. (6-38)

$$\sigma_t = \sigma_w \left(1 - \frac{r^2 + r_1^2}{2r^2} \ln \frac{r_3^2 - r_1^2}{r^2 - r_1^2} \right) \quad (6-41)$$

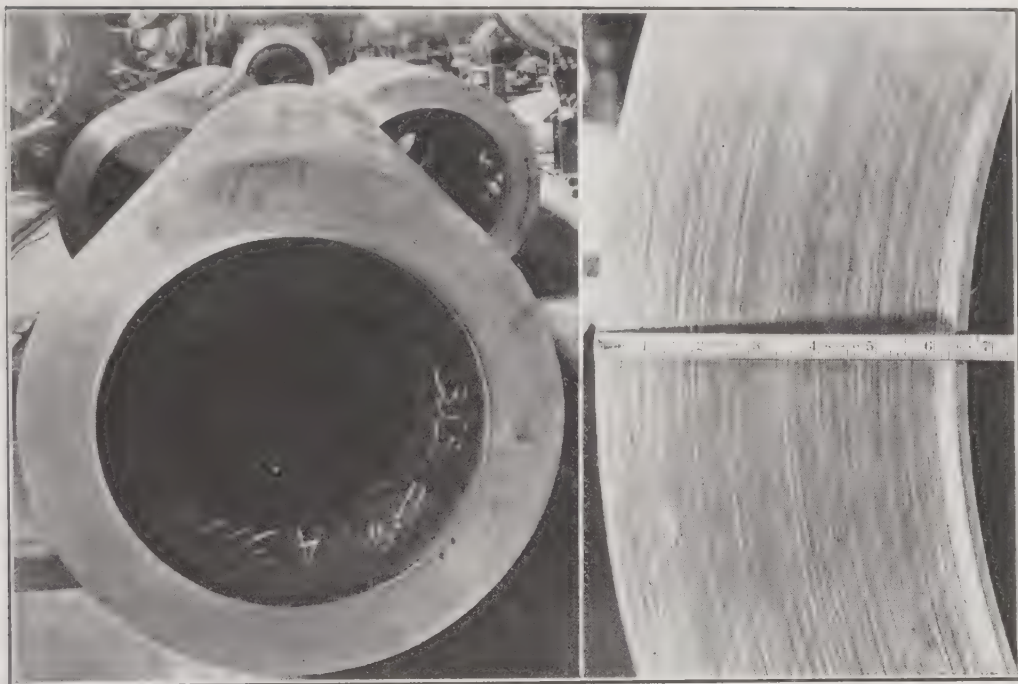
Equations (6-40) and (6-41) give the distribution of stresses in the winding when under zero internal and external pressure. The winding acts on the inner cylinder at r_2 with the radial stress

$$(\sigma_r)_{r_2} = - \frac{r_2^2 - r_1^2}{2r_2^2} \sigma_w \ln \frac{r_3^2 - r_1^2}{r_2^2 - r_1^2} \quad (6-42)$$

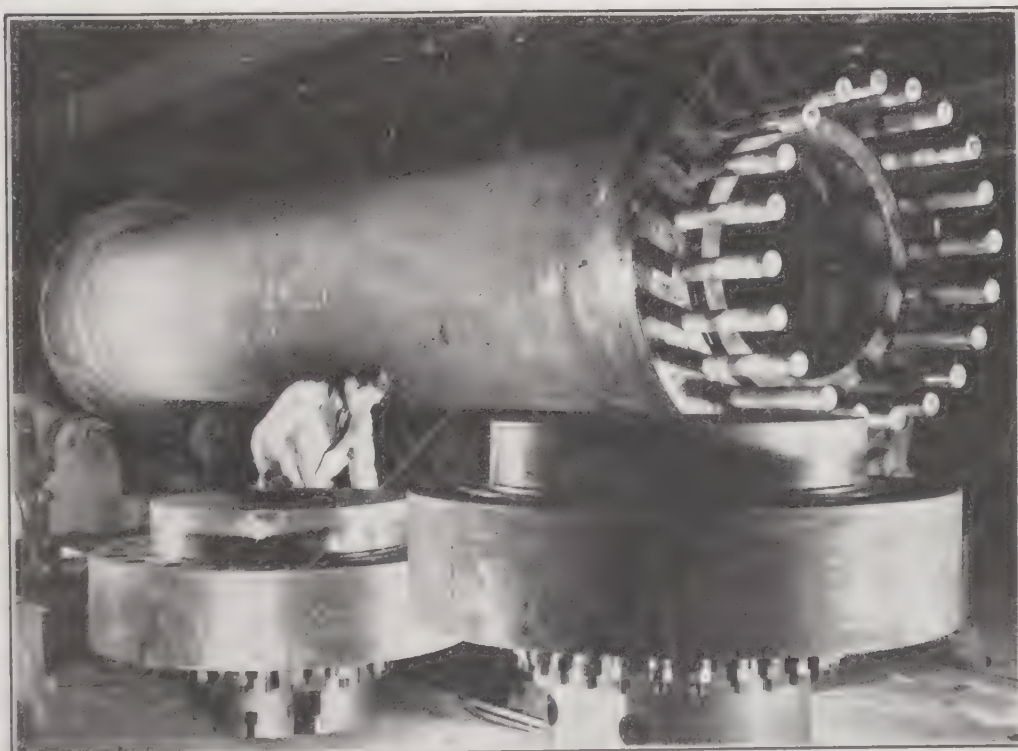
The stress distribution throughout the inner cylinder may be calculated from the equations for a simple cylinder subjected to the external pressure $p_2 = -(\sigma_r)_{r_2}$. The stresses in the cylinder under internal pressure p_1 may be obtained at any radius from r_1 to r_3 by first determining the stress in a simple cylinder at the radius r due to p_1 and then adding this to the stresses due to the winding calculated from Eqs. (6-40) to (6-42). With this method of winding, the stress in the winding is not constant when the cylinder is under the design pressure p_1' .

Jasper and Scudder⁵ describe the fabrication of thick-walled vessels by wrapping steel sheets, about $\frac{1}{4}$ in. thick, around a central core with the sheets applied under tension. A wall built up of layers in this fashion is shown in Fig. 6-6a. A completed vessel is shown in Fig. 6-6b. Over 7,500 vessels of this design have been built for service requiring pressures up to 12,500 psi. A vessel designed for 5,150 psi has a wall thickness of

⁵ T. M. Jasper and C. M. Scudder, *Trans. Am. Inst. Chem. Engrs.*, **37**:885 (1941); see also *A. O. Smith Corporation Bull.* V-53, Milwaukee, Wis.



(a)



(b)

FIG. 6-6. Multilayer walled vessels. (A. O. Smith Corporation.) (a) Wound cylinders. (b) Finished vessel.

8½ in., an inside diameter of 48 in., and a length of 45 ft. Only the inner corrosion-resistant layer is made gastight. Each of the other layers has small holes drilled through it and serves only to support the inner layer. If the inner layer is penetrated, by corrosion or otherwise, the pressure in the vessel subsides gradually. When tested to destruction, failure in the multilayer vessels occurred without shattering or fragmentation and with considerable deformation. Solid-walled vessels of comparable dimensions fragmented badly. This behavior is important from the standpoint of safety.

Layer construction also overcomes the limit to the size and weight of a forged pressure vessel imposed by the process of forging from a solid ingot. Each layer may be subjected to careful inspection, and this makes possible the accurate evaluation of the quality of the steel throughout the wall. The innermost layer, or core, may be chosen to resist corrosion or process conditions; and the outer layers, to resist the pressure and temperature of operation. It has already been pointed out that a solid-walled vessel constructed without prestressed walls will show unequal stress distribution through the wall. For a ratio of outer to inner diameters of 2, the metal on the outside is stressed only 40 per cent as much as that on the inside. If such a vessel could be constructed with uniform stress through the wall under operating conditions, the operating pressure could be 66 per cent greater at the same value of the maximum stress in the wall.

It is the general practice with forged vessels to stress-relieve them for several hours at elevated temperatures of the order of 1100°F. This treatment relieves stresses in the walls caused by the fabrication. One of the objects of the multilayer construction is to set up compressive residual stresses in the inner layers during fabrication which are later to be overcome by the operating pressure before these layers are subjected to tension. In order to preserve these residual stresses, stress-relieving is not practiced on the multilayer vessels. Jasper and Scudder⁵ report tests on two vessels constructed from the same sheets of steel cut in half. One was stress-relieved and the other was not. These were tested to the 0.2 per cent yield strength and to bursting. The vessel which was not stress-relieved held the advantage. The results are shown in Table 6-2.

In the multilayer construction just described, the layers also resist longitudinal stresses arising from the internal pressure acting on the heads of the vessel. This stress is never a limiting one in solid-wall construction. It becomes of major importance when the layers making up the wall thickness are applied as wire or ribbon rather than as sheets extending the length of the vessel. The former resist the stresses, set up by the internal pressure, acting radially on the walls of the vessel but not those acting longitudinally, and the inner core on which they

are wound must be of sufficient thickness to resist all the longitudinal stress.

Wickel-tape Walls. Holroyd⁶ describes a method developed in Germany by Schierenbeck⁷ for constructing a vessel wall by winding successive layers of steel tape on a central core. The tape is formed to close tolerances with grooves and lands. These interlock from layer to layer and enable the tape-wound wall to withstand longitudinal as well as radial and circumferential stresses. Vessels of this type have been built since 1938 on a production basis. About 50 vessels were made for testing purposes and 200 for plant service. Those for plant service are for

TABLE 6-2. STRESSES AT YIELD AND FAILURE OF TWO VESSELS†‡

Vessel	0.2% yield		Burst point	
	Pressure, psi	Stress, psi	Pressure, psi	Stress, psi
A.....	13,400	43,100	18,800	60,400 (not stress-relieved)
B.....	11,500	37,000	17,375	55,900 (stress-relieved)

† From T. M. Jasper and C. M. Scudder, *Trans. Am. Inst. Chem. Engrs.*, **37**:885 (1941).

‡ Twelve layers $\frac{1}{4}$ in. thick wrapped around an inside layer $\frac{1}{2}$ in. thick; wall thickness $3\frac{1}{2}$ in.; outside diameter 26 in.

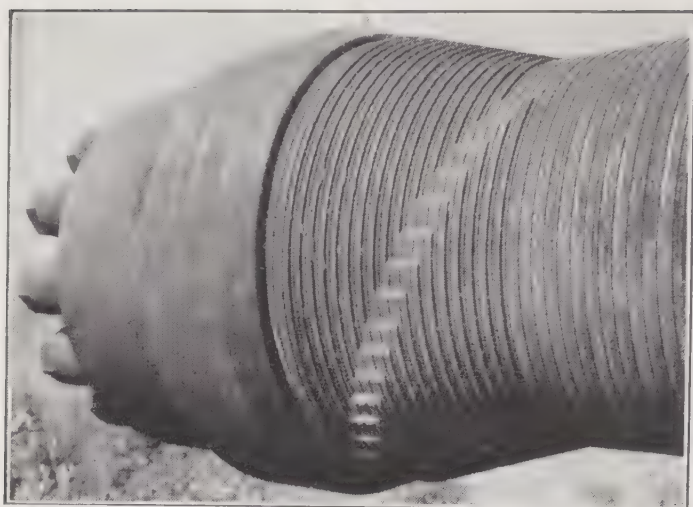
pressures up to 10,500 psi, and smaller sizes for research have been made for pressures up to 60,000 psi. The largest constructed by the end of World War II was a Tanol converter 59 ft long and 47.3 in. ID.

The flanged end of such a vessel is shown in Fig. 6-7a, and a longitudinal section through the inner tube and tape is shown in Fig. 6-7b. Wickel tape of two sizes has been used, 3.15 in. wide by 0.315 in. thick for the large vessels, and 1.97 in. wide by 0.197 in. thick for the smaller vessels. The number of layers of tape in any vessel must exceed a certain minimum. A spiral groove is machined on the surface of the inner tube, and the tape fits this groove snugly so that longitudinal movement is prevented.] Holroyd describes the process as follows:

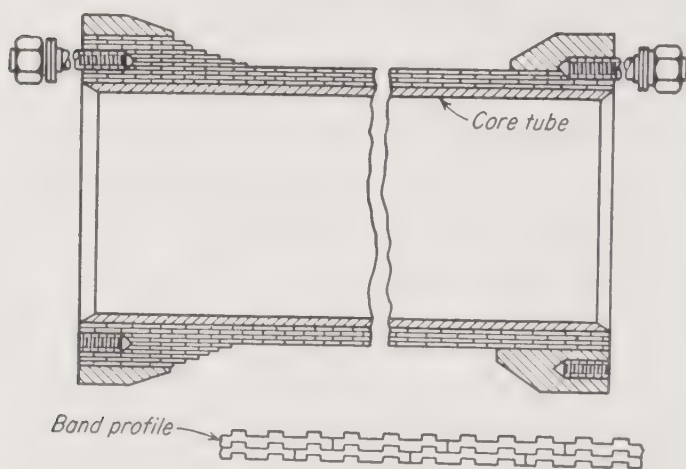
The process requires a lathe capable of taking the finished vessel and a large travelling bed to carry the tape spool and other equipment for handling the tape. A length of tape sufficiently long to wind one length of the vessel is first wound on the tape spool which is roughly 7 ft in diameter. These long lengths of tape are made by welding together a number of lengths as delivered to the plant by the tape makers. The free end is then welded on to the end of the vessel, and wind-

⁶ R. Holroyd, Report of Investigations by Fuels and Lubricants Teams, *U.S. Bur. Mines Inform. Circ.* 7375 (1946).

⁷ J. Schierenbeck, U.S. patent 326,176 (1943).



(a)



(b)

FIG. 6-7. Wickel-tape-wound cylinder. [From J. T. Donovan, M. Josenhaus, and J. A. Markovits, *Trans. ASME*, **72**:357 (1950), U.S. Department of Interior, Bureau of Mines.] (a) Flanged end. (b) Cross section.

ing begins. The tape, on its passage from the drum, passes between two rollers which act as one connection to a source of low voltage electric current. When the tape reaches the vessel, it is pressed on to it with a load of one ton by another roller which is grooved to fit the tape and acts as the other electrical connection. The current passing through the tape is about 4000 to 6000 amperes at 30 to 40 volts. Immediately before winding, the tape is thus heated to about 850°C. Immediately after the tape has been wound, it is cooled fairly rapidly by means of high velocity air jets and some distance later, about 5 to 6 turns of the tape, a series of water jets play on the tape to ensure that the vessel does not heat up. The intensity of this cooling depends on the rate of winding and the thickness of the tube. On completion of the winding of each layer of tape, the tape end is welded to the inner vessel or to the previous tape layer. The speed of winding can be as high as 15 ft per min.⁶

Figure 6-8 shows the arrangement of the winding lathe.⁸ The ends of the tape-wound cylinder are stiffened to receive the end closure. This is accomplished by using heavy, solid stiffening rings screwed to the ends or by building up the ends with additional layers of tape. The latter are secured by screwing on a thin ring. The ends of the wound tube, where the windings are welded together, are finally cut off, and only the interlocking of the layers of tape holds the turns in place. When winding gun barrels by this method, the tape is wound on under the proper tension to secure the desired distribution of stresses. Tests indicated

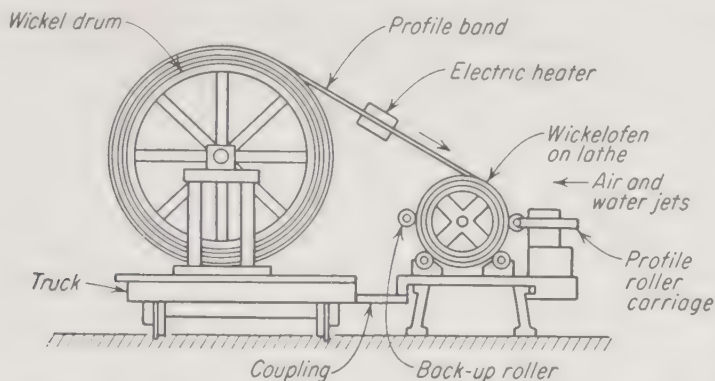


FIG. 6-8. Wickel-tape-wrapping lathe. [From J. T. Donovan, M. Josenhaus, and J. A. Markovits, *Trans. ASME*, **72**:357 (1950), U.S. Department of Interior, Bureau of Mines.]

that a wound vessel was 1.4 times as strong as a vessel with solid walls of the same dimensions. After stress-relieving at 700°C for one day, it was 1.2 times as strong.

Compound Cylinders. The stress concentration at the inner radius of a thick-walled vessel may be reduced and the stress distribution throughout the wall improved by shrinking an outer cylinder over an inner one.³ The surfaces of contact between these cylinders must be carefully machined. The outer cylinder is heated uniformly until it expands sufficiently to slip over the inner cylinder. If the inner diameter of the outer cylinder when cold is slightly less than the outer diameter of the inner cylinder, cooling and contraction will compress the inner cylinder and place its inner layers under residual compression, leaving the outer cylinder under tension. When the compound cylinder is subjected to an inner pressure, the initial compression in the inner walls is first reversed by the internal pressure, and the tension in the outer cylinder is increased. This results in a more uniform distribution of stresses.

A vessel may be constructed by shrinking on several such cylinders. The equations expressing the stresses in each of the three component directions for a duplex compound cylinder are given by Newitt.⁴ With

⁸ J. T. Donovan, M. Josenhaus, and J. A. Markovits, *Trans. ASME*, **72**:357 (1950).

two or more cylinders, the wall thickness of each cylinder should be chosen so that the thickness of the outer-cylinder wall is greatest and that of the inner least. The diameters of the cylinders should be in geometrical progression, that is, 1, 2, 4, 8, etc.

The advantage gained is greatest by shrinking on one outer cylinder, and the added advantage of a second outer cylinder is not so great. If more than one outer cylinder is contemplated, the multilayer type of construction should be considered as an alternative.]

Effect of Temperature Gradient. When a vessel is under pressure it will be weakened if subjected to a temperature which is excessive for the particular steel used in its construction. In addition to the weakening effect of high temperature, a temperature gradient through the wall will cause thermal stresses in the wall. These occur at lower temperatures and within the elastic limit of the steel. The thermal stresses due to a temperature gradient through the walls may be calculated. Temperature gradients are frequently encountered when heat from a reaction is removed through the vessel walls or when the contents of a vessel are heated from the outside. In the usual case, where the thermal conductivity is constant throughout the wall, the temperature distribution through the steel wall is given by

$$t = \frac{t_1 \ln (r/r_2) + t_2 \ln (r_1/r)}{\ln (r_1/r_2)} \quad (6-43)$$

Consider the case where stresses are set up in the walls of a cylindrical vessel when the temperature varies through the wall from t_1 at r_1 to t_2 at r_2 . The stresses due to this temperature gradient may be considered as separate from those caused by the internal pressure. To do this the internal pressure is considered zero. The stresses in a wall subjected to both an internal pressure and a temperature gradient may then be obtained by adding the two calculated separately. The steel, at any value of r , will expand radially, circumferentially, and longitudinally in accordance with the thermal coefficient of linear expansion α . The lower-temperature parts of the cylinder will expand less and will resist the expansion of the higher-temperature parts. This action sets up the thermal stresses.

If a point originally at radius r is displaced radially a distance δ , then the total unit strains in each direction due to thermal expansion and thermal stresses will be

$$\text{Radial strain} = \frac{d\delta}{dr} = \epsilon_r \quad (6-44a)$$

$$\text{Tangential strain} = \frac{2\pi\delta}{2\pi r} = \frac{\delta}{r} = \epsilon_t \quad (6-44b)$$

$$\text{Longitudinal strain} = \epsilon_z = \text{constant} \quad (6-44c)$$

The unit strain due to thermal expansion alone is αt , and the difference

between the total unit strain and the unit strain due to thermal expansion is that due to the temperature stresses. Therefore

$$\frac{d\delta}{dr} - \alpha t = \frac{1}{E} (\sigma_r - \nu\sigma_t - \nu\sigma_z) \quad (6-45a)$$

$$\frac{\delta}{r} - \alpha t = \frac{1}{E} (\sigma_t - \nu\sigma_r - \nu\sigma_z) \quad (6-45b)$$

$$\epsilon_z - \alpha t = \frac{1}{E} (\sigma_z - \nu\sigma_r - \nu\sigma_t) \quad (6-45c)$$

Equations (6-43), (6-45a), (6-45b), and (6-45c) may be combined with Eq. (6-2) and integrated. The thermal stresses are thus found to be

$$\sigma_r = \frac{E\alpha(t_2 - t_1)}{2(1 - \nu)} \left(\frac{K^2}{K^2 - 1} \frac{t_2 - t}{t_2 - t_1} + \frac{1}{K^2 - 1} \frac{t - t_1}{t_2 - t_1} - \frac{r_2^2/r^2}{K^2 - 1} \right) \quad (6-46a)$$

$$\sigma_t = \frac{E\alpha(t_2 - t_1)}{2(1 - \nu)} \left(\frac{K^2}{K^2 - 1} \frac{t_2 - t}{t_2 - t_1} + \frac{1}{K^2 - 1} \frac{t - t_1}{t_2 - t_1} + \frac{r_2^2/r^2}{K^2 - 1} - \frac{1}{\ln K} \right) \quad (6-46b)$$

$$\sigma_z = \frac{E\alpha(t_2 - t_1)}{(1 - \nu)} \left(\frac{K^2}{K^2 - 1} \frac{t_2 - t}{t_2 - t_1} + \frac{1}{K^2 - 1} \frac{t - t_1}{t_2 - t_1} - \frac{1}{2 \ln K} \right) \quad (6-46c)$$

The magnitude of these temperature stresses is shown in Fig. 6-9. This figure is for a cylinder with an inside diameter of 1.25 in., an outside diameter of 6.00 in., and a temperature difference of 235°C across the wall, from 250°C on one side to 15°C on the other side. Heat must flow continually through the wall to maintain this temperature gradient. When the heat flows from the inner to the outer wall, compressive circumferential stresses are set up on the inside of the vessel. When a fluid pressure is applied to the inside, these compressive stresses must be overcome before the inner layers are put under tension. A temperature gradient with the high temperature inside serves to equalize the stresses throughout the wall when the vessel is subjected to internal pressure. The vessel is therefore capable of withstanding a higher pressure, provided the increase in temperature does not weaken the steel.

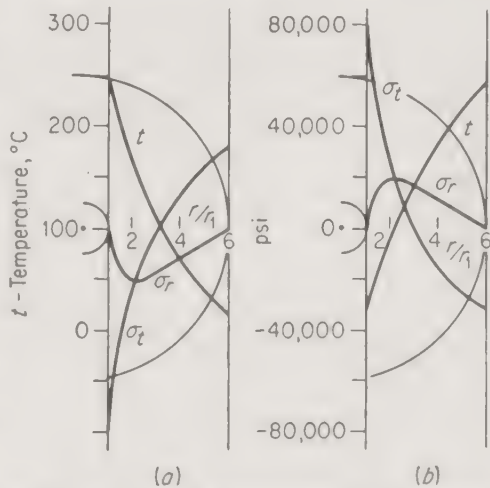


FIG. 6-9. Stress distribution in cylinder wall with a temperature gradient. (From D. M. Newitt, "Design of High Pressure Plant and Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.) (a) Heating the inside wall. (b) Heating the outside wall.

When the cylinder is heated from the outside, the inside layers are put under tension, the unequal stress distribution throughout the wall is accentuated, and the cylinder is weakened. Unlike the stresses caused by an internal pressure, the longitudinal stresses due to a temperature gradient are not constant throughout the wall.

In determining the combined stresses in the three directions due to pressure and temperature stresses, these are calculated independently of one another and then added. When calculating the strains due to these combined effects, the strains due to the combined pressure and temperature stresses are calculated first, and then the thermal-expansion strains are added. In many reactor designs where a high temperature is maintained inside the vessel, special provision is made to keep the inner walls of the vessel at a relatively low temperature. This is done by allowing the cool incoming gas to flow between the inner wall and an insulating layer. This design allows the use of a less costly steel, since the latter is not subjected to the high reaction temperatures.

Limits for Elastic Action—Stresses. The Lamé equations are for perfectly elastic deformation of all parts of the cylinder. These equations are valid within the range of elastic action. They cannot be used to determine the limiting stresses at which rupture occurs unless rupture and the limits of elastic action occur at the same stress. This is approximately true for cast iron and brittle material but not for most steels and ductile metal.

The limit of elastic action may be readily determined on a test specimen subjected to a simple tensile test in a testing machine. This information cannot be applied directly to an element in the walls of a thick-walled vessel. Under the latter condition, the specimen is subjected to stresses in three directions in comparison to one direction in the tensile test. A number of theories have been proposed for predicting the limit of elastic action in a massive wall from the limit measured in the simple tensile test. These will be discussed briefly. For more details the reader should consult standard texts.³ The maximum-octahedral-shearing-stress theory is accepted as the most reliable for ductile metals.

Maximum Energy of Distortion or Maximum-octahedral-shearing-stress Theory. Experiments on ductile metals⁹ have shown that this theory expresses the conditions under which these metals cease to behave elastically and become plastic at normal temperatures. The strain energy of distortion is obtained by subtracting the elastic energy of volume dilation from the total elastic energy of the solid. The strain energy of distortion is given by the expression

⁹ A. Nádai, "Theory of Flow and Fracture of Solids," McGraw-Hill Book Company, Inc., New York, 1950.

$$\frac{1 + \nu}{6E} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]$$

where σ_1 , σ_2 , and σ_3 are the three principal stresses. This value is constant for a given metal at the limit of elastic action for simple tension and for the three-dimensional stresses in a wall. For simple tension, where $\sigma_1 = \sigma_y$, it reduces to $\sigma_y^2(1 + \nu)/3E$. The relation between the three principal stresses and the tensile elastic limit is thus given by

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 2\sigma_y^2 = \text{a constant} \quad (6-47)$$

This theory by von Mises provides the criterion recommended for the limits to elastic action under the conditions normally encountered in the design of thick-walled cylinders.¹⁰

Maximum-shearing-stress Theory. This theory agrees approximately with the octahedral-shearing-stress theory. It holds that the breakdown of elastic action occurs when the shearing stress at any point due to any combination of stresses exceeds the shearing proportional limit of the material. When the principal stresses are of opposite sign, the maximum shear stress at any point is equal to one-half the algebraic difference between the maximum and minimum principal stresses. At any point in a thick-walled cylinder, the tangential stress is likely to be the largest, and the radial stress, in compression, will be the minimum stress. Under these conditions, the shearing stress will be one-half the sum of the tensile and compressive stresses. The shearing stress at any radius is then expressed by

$$\tau = \frac{K^2(p_1 - p_2)}{r^2(K^2 - 1)} \quad (6-48)$$

For a cylinder subjected to internal pressure only, the greatest shearing stress occurs at the inner wall, and this is along a plane at a 45° angle to the radial and tangential stresses. This theory is acceptable in most cases.

Maximum-principal-stress Theory. According to the maximum-principal-stress theory, any point in the body will cease to behave elastically when any one of the three principal stresses acting on it exceeds the stress at the elastic limit of the material in tension or compression as found in the simple tensile test. It is now known that this theory does not apply in general.

Maximum-strain Theory. The maximum-strain theory indicates that elastic action will cease at any point when the combination of stresses acting on this point causes a strain greater than that which occurred

¹⁰ A. Nádai, "Plasticity," McGraw-Hill Book Company, Inc., New York, 1931.

in the simple test specimen under tension or compression at the elastic limit. This theory also falls short of being realistic, and its use is not recommended.

Maximum-strain-energy Theory. When the simple test specimen is subjected to a tensile test, energy is expended upon it. This energy will increase as the strain increases, reaching a certain value at the elastic limit in simple tension. The maximum-strain-energy theory proposes that the energy absorbed per unit volume due to any combination of stresses at a point in the body must not exceed the energy per unit volume absorbed by the simple test specimen at its elastic limit. This theory is deficient in certain respects.

Other Stress Distributions. In the derivation of the Lamé equations, it was assumed that the longitudinal stress was uniformly distributed throughout the wall. It would be expected that near the ends of a vessel the distribution of these stresses would be other than uniform. However, a brief series of experiments by Cook and Robertson¹¹ indicates that this end effect extends only a very short distance from the end. In these experiments, a cylinder $\frac{5}{8}$ in. ID by $1\frac{1}{8}$ in. OD was cut into four lengths of 2.00, 4.25, 6.75, and 9.00 in. The tests made on these four cylinders showed practically no effect due to the length of the cylinders.

Unusual stress distributions are likely to occur around openings in the wall of a thick-walled cylinder and at points of sharp curvature. Special consideration should be given to the large concentration of stresses possible under these conditions. The treatment of such cases is outside the scope of this book.

6-2. Inelastic Behavior and Autofrettage. In the preceding text, only elastic deformation of the steel has been considered. The condition of a thick-walled cylinder and the relation between stresses and strains throughout the wall were discussed. Inelastic deformation will now be considered. The internal pressure just sufficient to cause inelastic action at the bore is called the *elastic-breakdown pressure*. A cylinder will withstand internal pressure considerably greater than that required to cause inelastic deformation of the inner layers of the cylinder wall. Inelastic deformation starts at the inner wall, and, as the internal pressure is increased above the elastic-breakdown pressure, the region of inelastic strains moves outward through the wall until it reaches the outer wall. The internal pressure just sufficient to cause inelastic action at the outer wall of the cylinder is called the *overstrain pressure*. The overstrain pressure is considerably higher than the elastic-breakdown pressure. Nádai⁹ develops the theory for these cases. An understanding of the behavior under these conditions enables one to predict the deformation

¹¹ G. Cook, *Proc. Inst. Mech. Engrs. (London)*, **126**:407 (1934).

of the inner wall, the overstrain pressure, and the effect of autofrettage. In autofrettage a pressure is applied which causes inelastic strains. This is then released, the cylinder is heat-treated, and the pressure is applied again. This is a technique used to increase the range of pressures which a vessel will withstand without inelastic deformation beyond that caused by the initial pressure treatment. It raises the elastic-breakdown pressure. Nádai¹⁰ discusses these conditions. Equation (6-2), for the equilibrium between the forces on an annular section of differential thickness in a thick-walled cylinder, is valid whether the strains are elastic or inelastic. Equation (6-4), however, does not apply when the strains are inelastic, but the assumption on which it was based—that the longitudinal strains are uniform throughout the wall thickness—applies equally well when the strains are inelastic. Equation (6-4) is replaced by an equation valid for inelastic strains by relating the stress to the inelastic strain. This is done by applying two conditions. The first is that the maximum-energy-of-distortion criterion of the limit of elastic action is applicable. The relation between the circumferential, radial, and longitudinal stresses at any point subjected to the limiting distortion energy is given by the von Mises yield condition [Eq. (6-47)]. The second condition is that over the small range of inelastic action usually involved, the energy of distortion remains constant and equal to its limiting value for elastic action. The limiting value of the energy of distortion is $(1 + \nu)\sigma_y^2/3E$. The second condition is valid for a substance having a stress-strain curve exhibiting a horizontal flat portion immediately following a well-defined yield point and applies only to the flat portion of the curve. If, further, the longitudinal strain ϵ_z is small compared to the strain in the other two directions ϵ_t and ϵ_r , then it can be shown that

$$\sigma_z = \frac{1}{2}(\sigma_t + \sigma_r) \quad (6-49)$$

$$\sigma_t - \sigma_r = \pm \frac{2}{\sqrt{3}} \sigma_y \quad (6-50)$$

Combining Eqs. (6-50) and (6-2) yields the differential equation

$$d\sigma_r = \pm \frac{2}{\sqrt{3}} \sigma_y \frac{dr}{r} \quad (6-51)$$

Integration of Eq. (6-51) leads to

$$\sigma_r = + \frac{\sigma_y}{\sqrt{3}} \left(\frac{r_2^2 - r_e^2}{r_2^2} + 2 \ln \frac{r_e}{r} \right) \quad (6-52a)$$

where r_e is the radius at the outer edge of the region of inelastic action. Combining Eq. (6-52a) with Eqs. (6-49) and (6-50) results in

$$\sigma_t = \frac{\sigma_y}{\sqrt{3}} \left(\frac{r_2^2 + r_e^2}{r_2^2} - 2 \ln \frac{r_e}{r} \right) \quad (6-52b)$$

$$\text{and} \quad \sigma_z = \frac{\sigma_y}{\sqrt{3}} \left(\frac{r_e^2}{r_2^2} - 2 \ln \frac{r_e}{r} \right) \quad (6-52c)$$

Equations (6-52a), (6-52b), and (6-52c) give the stresses in a thick-walled cylinder in the three directions in the region subjected to stresses sufficient to cause inelastic strains, where $r_1 \leq r \leq r_e$. No strain-hardening effects or residual stress due to cold-working or heat-treatment are included. If these are present, the stresses may be larger than indicated by these equations. The elastic-breakdown pressure may be found by substituting r_1 for both r and r_e in Eq. (6-25a), for at the inner wall the negative value of the radial stress is equal to the pressure. When internal pressure greater than the elastic-breakdown pressure is applied to a cylinder and is then released, the changes which occur are elastic, provided that certain parts of the cylinder are not stressed beyond the yield point in the opposite direction. The stresses throughout the wall of a cylinder undergoing only elastic strains may be calculated from the Lamé equations (6-6), (6-7), and (6-12). The cylinder with inelastic strains responds elastically when the internal pressure is released. The stresses calculated from Eqs. (6-6), (6-7), and (6-12) represent the change in stress at any point resulting from release of the internal pressure. When this change is added or subtracted, as the case may be, to the stress distribution existing when under pressure, the resulting stress distribution represents the residual stresses after the release of pressure. For example, a cylinder wall is subjected to the stress σ_t at the radius r as calculated from Eq. (6-52b). The residual stress at this point after the internal pressure is released may be obtained by subtracting the stress σ_t calculated from Eq. (6-6) from the stress calculated from Eq. (6-52b).

In Fig. 6-10 is shown the distribution of stresses throughout the wall of a cylinder with a ratio $r_2/r_1 = 2$ when subjected to the overstrain pressure. The distribution of stresses throughout the wall of the same cylinder at the elastic-breakdown pressure is shown in Fig. 6-2. Inelastic strain begins at the inner radius, and as the pressure is increased the zone of inelastic strain spreads and is bounded by a larger radius. The maximum circumferential stress is at the boundary between the elastic and inelastic region, and this stress is lower at all other radii. At the overstrain pressure the inelastic region has spread to the outer wall. The maximum circumferential stress then occurs at the outer wall, and not at the inner as is the case when all strains are elastic. Also, the longitudinal stress varies throughout the wall and is not constant. The stress distribution after the overstrain pressure is released is given in Fig. 6-11. Although both internal and external pressures are now zero, the outer

layers are subjected to a large circumferential tensile stress. The longitudinal stress also varies considerably throughout the wall. If the cylinder containing these residual stresses is again subjected to internal pressure, it will react elastically to all pressures up to that used to set up the residual stresses. This pressure range originally caused inelastic action. At higher pressures, inelastic action will take place. In relatively thick-walled cylinders with r_2/r_1 of the order of 2.5 or larger, the compressive stress at the inner surface set up by the release of the internal pressure may be great enough to cause reverse yielding. When this

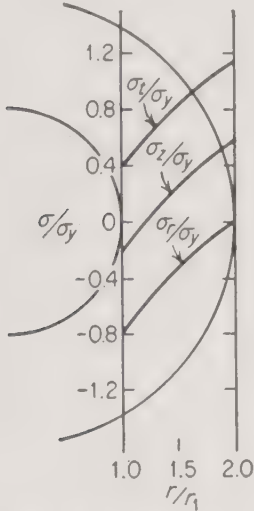


FIG. 6-10. Stress distribution in cylinder wall stressed to a plastic condition throughout by the overstrain pressure.

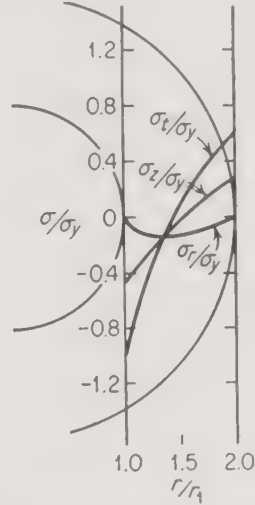


FIG. 6-11. Residual-stress distribution in cylinder wall after overstrain pressure used in Fig. 6-10 is released.

occurs, the behavior of the cylinder on the reapplication of pressure may not be elastic over the entire initial range of pressure. The occurrence of strain-hardening may further complicate the prediction of the behavior but usually results in greater cylinder strength.

Inelastic Strains. The strains resulting from elastic deformation of the walls of a cylinder may be calculated from Eqs. (6-15), (6-16), and (6-17). The inelastic strains may be calculated by recognizing that the volume of an element remains essentially constant as the inelastic strains are increased. Under these conditions, the sum of the three principal strains is zero.

$$\epsilon_r + \epsilon_t + \epsilon_z = 0 \quad (6-53)$$

Equations (6-44a), (6-44b), (6-44c), and (6-53) combine to give the differential equation

$$r d\delta + \delta dr = -\epsilon_z r dr \quad (6-54)$$

This may be integrated. Since ϵ_z , which is constant, is approximately

equal to $-\nu(\epsilon_t)_{r_2}$, the result simplifies to the form

$$\epsilon_t = (\epsilon_t)_{r_2} \left[\frac{r_2^2}{r^2} \left(1 - \frac{\nu}{2} \right) + \frac{\nu}{2} \right] \quad (6-55)$$

The circumferential strain ϵ_t is given as a function of the radius by this equation for the case when the inelastic region extends throughout the wall to the outer radius.

The strain at the outer surface at the overstrain pressure may be found¹² by using the von Mises yield condition, since the outer surface is at the limit of the elastic range and $\sigma_r = 0$. From Eqs. (6-16) and (6-17)

$$\sigma_t = \frac{E(\epsilon_t + \nu\epsilon_z)}{1 - \nu^2} \quad (6-56a)$$

$$\sigma_z = \frac{E(\epsilon_z + \nu\epsilon_t)}{1 - \nu^2} \quad (6-56b)$$

Substituting these in Eq. (6-47) results in

$$\sigma_y^2 = 4 \frac{E^2}{3} (\epsilon_z^2 + \epsilon_t^2 + \epsilon_t\epsilon_z) \quad (6-57)$$

However, σ_y can be expressed approximately as

$$(E\epsilon_y)^2 = \sigma_y^2 \quad (6-58)$$

and Eq. (6-57) becomes

$$(\epsilon_t)_{o_2} = \epsilon_y \frac{\sqrt{3}}{2} \left[\frac{1}{\sqrt{(\epsilon_z/\epsilon_t)^2 + \epsilon_z/\epsilon_t + 1}} \right] \approx 0.866\epsilon_y \quad (6-59)$$

since the expression in brackets is near unity in many cases.

The magnitude of the strains may be illustrated by considering a cylindrical vessel constructed of steel having a tensile yield strength of 90,000 psi, with $r_2/r_1 = 1.5$ and $\nu = 1/3$. When this cylinder is subjected to the overstrain pressure,

$$\frac{(\epsilon_t)_{r_1}}{(\epsilon_t)_{r_2}} = 2.04$$

The circumferential strain at the outer surface when yielding starts is obtained as follows: $\epsilon_y = 90,000/30 \times 10^6 = 0.003$ in./in., and

$$(\epsilon_t)_{r_2} = 0.866 \times 0.003 = 0.0026.$$

$(\epsilon_t)_{r_1} = 2.04 \times 0.0026 = 0.53$ per cent. With this steel and $r_2/r_1 = 2$,

¹² J. H. Faupel and A. R. Furbeck, *Trans. ASME*, **75**:345 (1953); see also J. H. Faupel, *J. Franklin Inst.*, **259** (5):405 (1955), and J. H. Faupel, Paper 55-PET-1, presented at the ASME Petroleum Conference, Sept. 25 to 28, 1955.

when the inelastic strain has just spread through the wall the strain at the inner wall is about 1 per cent and 3.5 times the limiting elastic strain. The overstrain pressure under these conditions is nearly double the elastic-breakdown pressure.

The elastic-breakdown pressure and the overstrain pressure for solid walls and the elastic-breakdown pressure for multilayer walls are compared in Fig. 6-12. The external pressure is zero, and the ratio of the internal pressure to the tensile elastic limit is shown vs. the ratio of outer to inner radius. The lower curve indicates the conditions in a solid-walled cylinder at the elastic-breakdown pressure, or when inelastic strains are just beginning at the inner surface. The conditions in the same cylinder at the overstrain pressure, or when inelastic strains have spread throughout the wall and have just reached the outer surface, are shown on the higher curve. The highest line is for a wall constructed of properly prestressed layers when subjected to a pressure sufficient to cause a uniform elastic strain throughout the wall so that the entire wall is strained to the limiting elastic value.

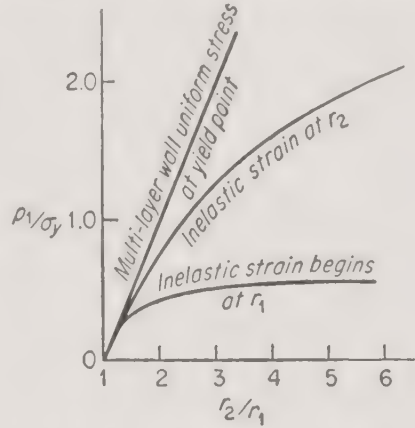


FIG. 6-12. Ratio of internal pressure to tensile yield strength required to cause inelastic strain. (From F. B. Seely and J. O. Smith, "Advanced Mechanics of Materials," John Wiley & Sons, Inc., New York, 1952.)

Residual Stresses. Residual stresses are found in the thick walls of a cylinder when it is subjected to prestressing as in the autofrettage treatment. Faupel and Furbeck¹² discuss the influence of residual stresses on the behavior of cylinders and point out that such stresses also occur as a result of heat-treatment. Equations such as (6-47), (6-52a), (6-52b), and (6-52c) do not make allowance for the presence of the residual stresses which may exist when the cylinder is not subjected to an internal pressure. The effect of residual stresses on the elastic-breakdown pressure may be accounted for by introducing the appropriate residual stresses present at the inner wall of the cylinder into the von Mises yield condition as given by Eq. (6-47). There is no radial residual stress at the inner wall, and only circumferential and longitudinal residual stresses need be considered. For application at the bore, Eq. (6-47) becomes

$$2\sigma_y^2 = (\sigma_t + \sigma'_t - \sigma_r)^2 + (\sigma_r - \sigma_z - \sigma'_z)^2 + (\sigma_z + \sigma'_z - \sigma_t - \sigma'_t)^2 \quad (6-60)$$

For an internal pressure p_1 ($p_2 = 0$) in a closed-end cylinder, the stresses σ_t , σ_r , and σ_z at the bore are found from Eqs. (6-6), (6-7), and (6-12) to be $p_1(K^2 + 1)/(K^2 - 1)$, $-p_1$, and $p_1/(K^2 - 1)$, respectively. Substitut-

ing these values into Eq. (6-60) leads to

$$p_y^2 \left(\frac{K^2}{K^2 - 1} \right)^2 + p_y \left(\frac{K^2}{K^2 - 1} \right) \sigma'_t + \frac{1}{3} (\sigma_z'^2 + \sigma_t'^2 - \sigma'_z \sigma'_t - \sigma_y^2) = 0 \quad (6-61)$$

Equation (6-61) may be solved for the elastic-breakdown pressure p_y . If no residual stress is present, σ'_t and σ'_z are zero and this equation reduces to

$$p_y = \frac{\sigma_y}{\sqrt{3}} \frac{K^2 - 1}{K^2} \quad (6-62)$$

Faupel and Furbeck¹² measured the residual stresses and the elastic-breakdown pressures in a number of cylinders. The elastic-breakdown pressures calculated from Eq. (6-61) agreed within ± 15 per cent with the measured values, but, when the residual stresses were not allowed for, errors of over 50 per cent were obtained.

The measured values of the overstrain pressure p_o agreed fairly well with the values predicted by the von Mises criterion, which from Eq. (6-52a) for overstrain of heavy-walled cylinders is

$$p_o = \frac{2\sigma_y}{\sqrt{3}} \ln K \quad (6-63)$$

At the outer surface of a cylinder subjected to the overstrain pressure p_o , $\sigma_r = 0$, $\sigma_z = p_o/(K^2 - 1)$, and from Eq. (6-49) $\sigma_t = 2p_o/(K^2 - 1)$. Substituting these values in Eq. (6-16) gives the strain at the outer surface at elastic breakdown

$$(\epsilon_t)_{o2} = \frac{p_o(2 - \nu)}{E(K^2 - 1)} \quad (6-64)$$

The strain at the bore at the elastic-breakdown pressure is

$$(\epsilon_t)_{y1} = \frac{p_y}{E(K^2 - 1)} [(K^2 + 1) + \nu(K^2 - 2)] \quad (6-65)$$

The strain at the bore is found from the geometry to be related to that at the surface as follows,

$$\epsilon_{t1} = K^2 \epsilon_{t2} \quad (6-66)$$

From Eq. (6-59), at the overstrain pressure,

$$(\epsilon_t)_{o1} = 0.866 \epsilon_y K^2 \quad (6-67)$$

6-3. Bursting. A pressure in excess of the overstrain pressure is usually required to burst a cylinder. The following formula for predicting the bursting pressure is consistent with the assumptions used for predicting the elastic-breakdown and overstrain pressures.

It is postulated that, if the cylinder yields at constant stress, as stated by classical plasticity theory, it will burst at the pressure required to overstrain the wall, that is, the lower limit will be

$$(p_b)_i = \frac{2\sigma_y}{\sqrt{3}} \ln K \quad [6-68]$$

If the tensile yield strength σ_y is equal to the tensile ultimate strength σ_u , bursting will occur at a pressure defined by the relation

$$(p_b)_k = \frac{2\sigma_u}{\sqrt{3}} \ln K \quad (6-69)$$

However, when the yield strength is less than the ultimate strength, the bursting pressure will be somewhere between the pressures defined by Eqs. (6-68) and (6-69).

Consequently, it is postulated that the bursting pressure will be a function of both the overstrain pressure [Eq. (6-68)] and the pressure defined by [Eq. (6-69)]. Thus assuming direct proportionality $[(p_b)_i \propto \sigma_y/\sigma_u]$, and $(p_b)_k \propto 1 - \sigma_y/\sigma_u]$

$$p_b = \left(2 - \frac{\sigma_y}{\sigma_u}\right) \frac{2\sigma_y}{\sqrt{3}} \ln K \quad [6-70]$$

Thus, according to [Eq. (6-70)], if σ_y/σ_u were unity, then $\sigma_y = \sigma_u$ and

$$p_b = \frac{2\sigma_u}{\sqrt{3}} \ln K \quad [6-71]$$

which is consistent with the foregoing reasoning.¹²

The entire cylinder wall has yielded and is in a plastic condition before bursting occurs. The prediction of the strain at the bursting pressure is a complex problem unless some simplifying assumptions are made. To provide a theory of failure it is postulated that failure will occur in the cylinder when the bore strain reaches the value of the strain at the ultimate stress in tension. Therefore, the bore circumferential strain at failure is given by the relation

$$(\epsilon_t)_{b1} = \epsilon_u \quad (6-72)$$

and, by the geometry of the cylinder, the circumferential strain at failure at the outside of the cylinder is

$$(\epsilon_t)_{b2} = \frac{\epsilon_u}{K^2} \quad (6-73)$$

6-4. Experimental. A number of cylinders were subjected to internal pressure by Faupel and Furbeck,¹² and the behavior of the cylinders was compared with that predicted by the above methods. Three cylinders of each material were treated under identical conditions. The residual

TABLE 6-3. DESCRIPTION OF CYLINDERS AND ELASTIC-BREAKDOWN PRESSURES^{1,2}

Cylinder	Material	Treatment		Properties in transverse direction at bore of cylinder			Wall ratio, K	Residual stress at bore, psi		External circumferential strain at elastic breakdown, $\mu\text{in./in.}$	Elastic-breakdown pressure, psi		Error based on observed value, %	
				Yield strength, psi		Ultimate strength, psi								
		Thermal	Processing	0.01 % offset	0.20 % offset			Longitudinal	Circumferential		Observed	Eq. (6-61)	Eq. (6-62)	
1	Cr-Ni-Mo-V steel (0.35 C, 0.7% Mn, 0.48 Ni, 1.39 Cr, 0.13 V, 0.52 Mo, 0.20 Si)	Heated at 1525°F, cooled to 750°F at rate of 30°F/ hr and from 750°F to room temperature in air at uncontrolled rate	Treated as solid 3-in.-OD bar and machined to 1.00 in. ID by 2.75 in. OD	47,000	47,800	93,100	2.74	0	0	180	21,000	23,500	23,500	12
2	Same as cylinder 1	Heated at 1600°F for 3 hr, quenched in oil, drawn at 1000°F for 3 hr, and quenched in water	Same processing as cylinder 1	141,200	159,800	177,500	2.74	0	0	620	70,000	70,800	70,800	1
3	SAE 3320 steel (0.23 C, 0.35 Mn, 3.60 Ni, 1.62 Cr, 0.03 Mo, 0.49 Si)	Heated at 1580°F for 4 hr, quenched in oil, drawn at 970°F for 4 hr, air-cooled, redrawn at later date at 1200°F for 4 hr, and quenched in water	Treated as solid 4.5-in.-OD bar and machined to 1.50 in. ID by 4.125 in. OD	74,300	79,500	105,400	2.74	45,000	35,000	185	21,000	19,400	37,150	77
4	SAE 4340 steel (0.40 C, 0.75 Mn, 1.87 Ni, 0.77 Cr, 0.26 Mo, 0.27 Si)	Heated at 1600°F, quenched in oil, drawn at 1200°F, and furnace cooled	Same processing as cylinder 3	99,400	103,900	124,100	2.75	0	0	400	45,000	49,800	49,800	11
5	SAE 4340 steel	Heated at 1650°F, air- cooled, drawn at 1200°F, and quenched in water	Same processing as cylinder 3	83,400	86,500	115,300	2.75	0	0	390	43,700	41,800	41,800	-4
6	SAE 4340 steel	Heated at 1650°F, air- cooled, drawn at 1200°F, and furnace-cooled	Treated as solid 2-in.-OD bar and machined to 0.50 in. ID by 1.25 in. OD	119,600	115,600 ¹	124,600	2.50	32,000	26,000	450	42,500	44,500	56,000	10
														31

TABLE 6-3. DESCRIPTION OF CYLINDERS AND ELASTIC-BREAKDOWN PRESSURES (Continued)

Cylinder	Material	Treatment		Properties in transverse direction at bore of cylinder			Wall ratio, K	Residual stress at bore, psi		External circumferential strain at elastic breakdown, $\mu\text{in./in.}$	Elastic-breakdown pressure, psi		Error based on observed value, %	
				Yield strength, psi	Ultimate strength, psi	Longitudinal		Circumferential	Observed†		Calculated			
Thermal	Processing	0.01 % offset	0.20 % offset							Eq. (6-61)	Eq. (6-62)			
7	SAE 1045 steel (0.45 C, 0.70 Mn, 0.23 Si)	Heated at 1600°F, quenched in oil, drawn at 800°F, and furnace-cooled	Treated as plugged-end hollow cylinder 1.25 in. ID by 4.5 in. OD and machined to 1.50 in. ID by 4.125 in. OD	57,500	60,900	101,800	2.75	20,000	20,000	195	21,300	20,300 28,800	-5	35
8	Same as cylinder 7	Same as cylinder 7	Treated as hollow cylinder 1.25 in. ID by 4.5 in. OD, quenched by immersing bar in oil and simultaneously inserting a perforated pipe through bore for bore quenching by oil under pressure, and machined to 1.50 in. ID by 4.125 in. OD	76,800	81,600	122,200	2.75	-37,000	-34,000	490	57,500	55,300 38,500	-4	-33
9	SAE 1035 steel	Annealed	39,950	38,600	73,100	2.75							
10	SAE 3320 steel	Annealed	58,100	68,500	112,600	2.75							
11	Cr-Ni-Mo-V steel	Annealed	45,100	45,300	83,300	2.75							

† The observed elastic-breakdown pressures are taken as those pressures on the curve of pressure vs. external circumferential strain where departure from linearity occurs.

‡ Lower yield point—used in calculations for data in tables.

TABLE 6-4. OBSERVED AND CALCULATED VALUES

Cylinder	Overstrain pressures				$\frac{\sigma_y}{\sigma_u}$	Bursting pressures			Error based on observed value, %
	External circumferential strain at overstrain, $\mu\text{in.}/\text{in.}$	Observed overstrain pressure, psi	Calculated overstrain pressure, Eq. (6-63), psi	Error based on observed value, %		Approx. external circumferential strain at bursting, $\mu\text{in.}/\text{in.}$	Bursting pressure, psi		
							Observed	Calculated, Eq. (6-70)	
1	1,550	58,000	54,400	-7	0.505	19,000	100,000	81,500	-19
2	4,000	200,000	163,800	-18	0.796	>200,000	192,200	
3	2,200	84,000	86,200	3	0.700	15,000	106,000	111,800	5
4	3,600	117,000	115,200	-2	0.800	17,000	133,000	138,500	4
5	2,950	99,000	97,200	-2	0.720	16,000	120,000	124,200	4
6	3,335	111,000	122,100	10	0.940	9,000	117,000	129,400	11
7	2,025	66,500	67,000	1	0.564	20,000	107,000	96,100	-10
8	2,335	87,750	86,500	2	0.630	19,000	119,000	122,700	3

stresses were determined in one cylinder. Another was used to determine the mechanical properties resulting from heat-treatment as well as to provide material for microscopic examination. The third was subjected to a static internal-pressure test. For example, a $1\frac{1}{2}$ -in.-ID by 36-in.-long cylinder was equipped with 20 strain gauges on the outer surface

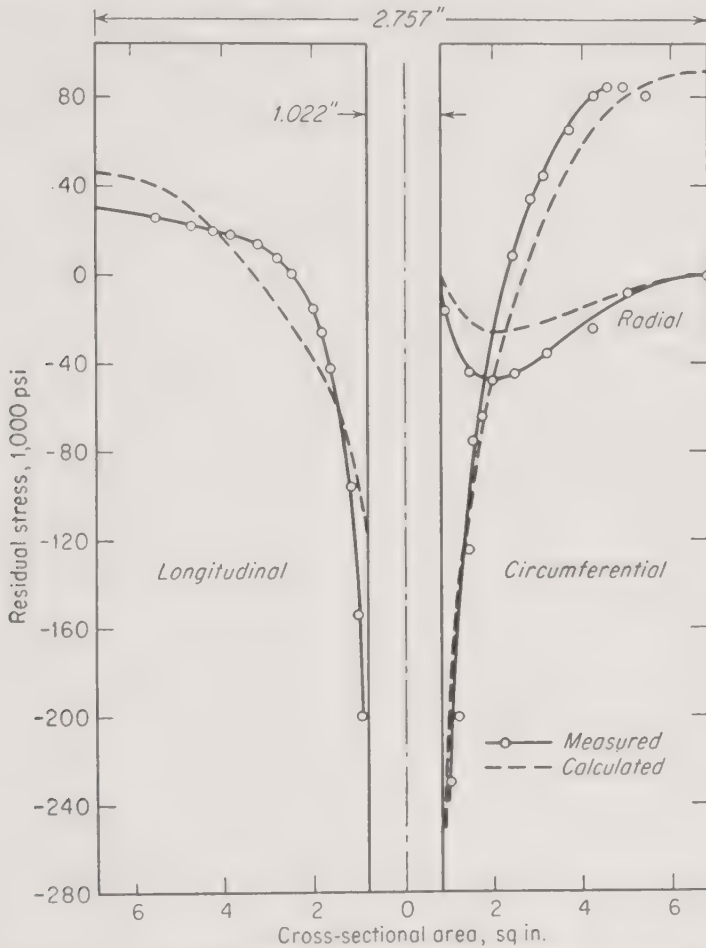


FIG. 6-13. Comparison of calculated and measured residual-stress distributions in autofrettaged heat-treated Cr-Ni-Mo-V cylinder. [After J. H. Faupel and A. R. Furbeck, *Trans. ASME*, **75**:345 (1953).]

for the pressure test. Residual stresses were determined by the procedure developed by Sachs.¹³

The materials used and their thermal treatment are shown in Table 6-3 together with the processing of the cylinders, the properties at the bore zone, and the observed and calculated elastic-breakdown pressures. The observed and calculated overstrain pressures and bursting pressures are listed in Table 6-4. These results indicate that predictions can be made

¹³ G. Sachs, "Symposium on the Failure of Metals by Fatigue," pp. 237-247, Melbourne University Press, Melbourne, Australia, 1947.

within ± 15 per cent when allowance is made for the bore residual stresses. Errors greater than 50 per cent were found when such allowance was not made. Residual stresses in cylinders due to heat-treatment do not appear to influence overstrain or bursting pressures, but for operation within the elastic range a knowledge of the residual stresses is required.

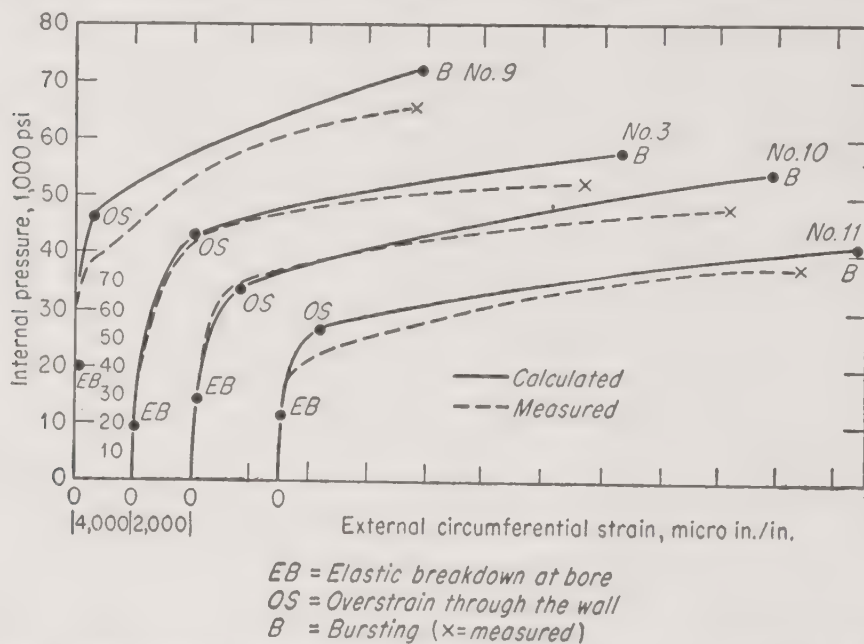


FIG. 6-14. Pressure-strain curves for heavy-wall cylinders under internal pressure. [After J. H. Faupel and A. R. Furbeck, *Trans. ASME*, **75**:345 (1953).]

A comparison of the predicted and measured residual stresses in an autofrettaged heat-treated cylinder is shown in Fig. 6-13. The complete pressure-strain curves as measured for four cylinders are compared with the calculated curves in Fig. 6-14. More precise methods for making the calculations have been proposed by MacGregor;¹⁴ however, for engineering purposes, the methods described here are satisfactory. Other authors^{10,15-18} have treated the plasticity of metals. Warren¹⁹ discusses the autofrettage process as applied to gun tubes.

¹⁴ C. W. MacGregor, L. F. Coffin, Jr., and J. C. Fisher, *J. Appl. Phys.*, **19**:291 (1948).

¹⁵ R. Hill, "The Mathematical Theory of Plasticity," chap. 5, Oxford University Press, New York, 1950.

¹⁶ C. W. MacGregor, L. F. Coffin, Jr., and J. C. Fischer, *J. Franklin Inst.*, **245**(2): 135-358 (1948).

¹⁷ A. C. Macrea, "Overstrain of Metals" (His Majesty's Stationery Office, London, 1930).

¹⁸ C. F. Jeansen, "A Treatise on Radial Expansion of Guns," Navy Department, Washington, 1938.

¹⁹ A. G. Warren, in "Symposium on Internal Stresses in Metals and Alloys," pp. 209-218, The Inst. of Metals, London, 1948.

NOMENCLATURE

E	Modulus of elasticity $\sigma = E\epsilon$
g	Local acceleration due to gravity, ft/sec ²
g_c	Conversion factor, 32.1740 (lb mass)(ft)/(lb force)(sec ²)
h	Thickness of each layer in a multilayer wall
K	r_2/r_1
K_1	r_2/r_1 (see Fig. 6-3)
K_2	r_3/r_1 (see Fig. 6-3)
m	Number of a designated layer counted from bore
n	Number of total wound layers counted from bore
p_b	Bursting pressure in cylinder, psi
$(p_b)_l$	Lower limit of bursting pressure in cylinder, psi
$(p_b)_u$	Upper limit of bursting pressure in cylinder, psi
p_1	Gauge pressure on inner wall of a cylinder, psi
p_2	Gauge pressure on outer wall of a cylinder, psi
p_1'	Specified value of internal pressure, psi
p_2'	Pressure equivalent to radial stress of wound layer on inner cylinder when internal pressure is p_1' , psi
p_o	Overstrain pressure, psi
p_m	Wrapping pressure or external pressure on each layer due to next single layer as it is applied
r	Radial distance from the axis to a point in a cylinder; r_1 , inside radius; r_2 , outside radius of solid wall; r_3 , outside radius of second cylinder in compound wall (see Fig. 6-3)
r_c	Radius at boundary between elastic and plastic zones in cylinder wall
t	Temperature, °F or °C; also thickness of cylinder wall
t_1	Temperature at r_1 in a cylinder wall
t_2	Temperature at r_2 in a cylinder wall
x_1, x_2	Radii to mid-thickness of each wound layer
α	Coefficient of linear expansion
δ	The radial displacement of a point in a cylinder wall due to strain; δ_1 at the inner surface, δ_2 at the outer surface
ϵ	Strain; elongation per unit length
ϵ_r	Strain in radial direction
ϵ_t	Strain in tangential, circumferential, or hoop direction
$(\epsilon_t)_{u1}$	Circumferential strain at bore of cylinder at elastic-breakdown pressure, in./in.
$(\epsilon_t)_{o1}$	Circumferential strain at bore at overstrain pressure, in./in.
$(\epsilon_t)_{o2}$	Circumferential strain at outer surface of cylinder at overstrain pressure, in./in.
$(\epsilon_t)_{b1}$	Circumferential strain in cylinder at bore at bursting pressure, in./in.
$(\epsilon_t)_{b2}$	Circumferential strain in cylinder at surface at bursting pressure, in./in.
ϵ_z	Strain in axial or longitudinal direction
ϵ_u	Strain in tension at ultimate strength, in./in.
ϵ_y	Strain in tension at 0.01 per cent offset yield strength, in./in.
ν	Poisson's ratio

- σ Stress, psi; tension is positive, compression is negative
- σ_r Stress in radial direction, psi; $(\sigma_r)_{r_1}$, at inside radius
- σ_t Stress in tangential, circumferential, or hoop direction, psi; $(\sigma_t)_{r_1}$, at inside radius
- σ'_t Residual circumferential stress in cylinder, psi
- σ''_t Constant circumferential stress throughout a wound layer, psi
- σ_{t_a} Allowable working stress
- σ_{t_c} Limiting allowable stress
- σ_{t_r} Circumferential stress at r due to outside layers alone from r to r_3
- σ_z Stress in longitudinal or axial direction, psi
- σ'_z Residual longitudinal stress in cylinder, psi
- σ_w Tension in the wire or tape during the winding operation
- σ_1 A principal stress; σ_2 and σ_3 , the other principal stresses
- σ_u Ultimate tensile strength, psi
- σ_y Yield strength in tension at 0.2 per cent offset (used to calculate p_b), psi; or 0.01 per cent offset (used to calculate p_y)
- τ Shearing stress, psi

CHAPTER 7

EXPERIMENTAL TECHNIQUES

The experimental techniques for making measurements under high-pressure conditions are too numerous to permit a discussion of all of them. A selected few will be described. The pressure, volume, and temperature of a known mass of fluid are frequently measured. These measurements are called pVT data. If the fluid separates into two phases—gas and liquid—the volume, density, and composition of each phase are desirable information. Such measurements are phase-equilibrium data. A number of properties of a fluid can be calculated from pVT data by methods based on the laws of thermodynamics. The changes in heat capacity with pressure can be calculated in this way, but the results under some conditions are of limited precision. Thus, the heat capacity is sometimes measured directly at high pressures. Viscosity, thermal conductivity, and molecular diffusivity are examples of the transport properties of a fluid. These are measured directly. Present knowledge does not enable one to predict the rates of chemical reactions, and these are measured under numerous conditions, sometimes at elevated pressure. The techniques employed to measure these quantities are of interest to the chemical engineer.

7-1. Pressure, Volume, Temperature. Instruments and techniques for measuring pressure, volume, and temperature have been developed to yield values of high precision. Fewer complications are encountered in making these measurements than in making many others. pVT measurements are among the most basic and the most useful when information is sought as to the behavior of a substance. These precise measurements are used in the calculation of other properties such as the energy, enthalpy, entropy, and the like. These calculations are based on rigorous methods derived from thermodynamics.

There are two general measuring procedures. One is the *variable-volume method* which has been developed from the pioneer work of Amagat.¹ A vessel is arranged with a variable volume by introducing mercury or by using a piston. The volume is measured at several positions of the mercury or piston. With the vessel in a constant-

¹ E. H. Amagat, *Ann. chim. et phys.*, **29**(6):68 (1893).

temperature bath, a known quantity of gas is then introduced. The pressure is observed at each of the several known volumes, and several combinations of pVT conditions may be read with one filling of the vessel.

The other procedure is the *constant-volume method*. A vessel with a fixed volume is used. This volume is measured and then an unknown quantity of gas at a high pressure is introduced. The vessel is held at a constant temperature until the temperature and concentration are uniform throughout the volume. Observation of the pressure, volume, and temperature provides one combination of pVT conditions. The quantity of gas in the vessel is determined by allowing it to expand to a large known volume so as to observe another pVT combination. In the large volume the pressure is low so that the mass of gas can be determined from previous measurements or from the gas laws. Only a single pVT combination is observed with one filling, but the simplicity of construction and operation of the apparatus is a compensating factor.

When pVT data are used in the calculation of thermal properties, the methods require the determination of certain derivatives (or slopes), giving, for instance, $(dp/dV)_T$, the change in pressure with volume at constant temperature. These derivatives cannot be evaluated with the same precision as the original pVT measurements. For such calculations a high order of precision is desirable in the pVT measurements in order to preserve a reasonable precision in the calculated properties.

Variable-volume Method. Among the most precise pVT measurements are those by Michels^{2,3} and his co-workers, who used this method at pressures up to 3,000 atm. Variations of the method have also been used by others, Benedict⁴ to 6,000 atm, Bridgman⁵ to 15,000 atm, Smith and Taylor,⁶ and Sage and Lacey and their co-workers.^{7,8,9} Hagenbach's variation of Michels's apparatus will illustrate this method. It consists of four main parts: a dead-weight pressure gauge, a glass piezometer, a steel pressure bomb, and a constant-temperature bath. Auxiliary apparatus includes oil injectors, Bourdon pressure gauges, and mercury manometers. A second glass piezometer is required to provide enough

² A. Michels, C. Michels, and H. Wouters, *Proc. Roy. Soc. (London)*, **153A**:214 (1935).

³ A. Michels and R. Gibson, *Ann. Physik*, **87**:850 (1928).

⁴ M. Benedict, *J. ACS*, **59**:2224, 2233 (1937).

⁵ P. W. Bridgman, "The Physics of High Pressure," The Macmillan Company, New York, 1931.

⁶ L. B. Smith and R. S. Taylor, *J. ACS*, **47**:3122 (1925).

⁷ B. H. Sage and W. N. Lacey, *Am. Inst. Mining Met. Engrs. Tech. Publ.* **1127** (1939).

⁸ B. H. Sage, *Am. Inst. Mining Met. Engrs. Tech. Publ.* **2269** (1947); *Petroleum Technol.*, **10**(5) (1947).

⁹ B. H. Sage, D. C. Webster, and W. N. Lacey, *Ind. Eng. Chem.*, **29**:658 (1937).

measurements in the intermediate pressure ranges for subsequent calculations from the pVT data. The glass piezometer is the variable-volume vessel. As shown in Fig. 7-1, it consists of a number of glass bulbs of varying size connected by capillary tubing. A fine platinum wire is fused into each piece of capillary tubing and serves as an electric contact. The volume above each contact to the top of the piezometer is found by weighing the mercury required to fill it. This volume calibration is repeated at each temperature where pVT measurements are to be made.

For measurements at high pressures, the glass piezometer is enclosed in the steel pressure bomb. The pressures inside and outside the glass vessel are balanced so that the net pressure differential across the glass is small when the gas sample is subjected to as much as 3,000 atm. Mercury fills the lower part of the steel bomb and rises into the piezometer to reduce the volume of the sample gas. The position of the mercury is indicated when it touches a platinum contact which is connected to a suitable electric circuit. This position determines the volume. The temperature is measured in the bath. The pressure is measured in the bomb through a connection in its side to the dead-weight gauge. The upper part of the steel bomb above the mercury is filled with oil, and an oil injector introduces more oil into the bomb through the same connection used to measure the pressure. This raises the pressure on the mercury, forcing it to a higher level in the piezometer. A connection in the bottom of the bomb is used to introduce the sample gas. It is shut off during measurements. This connection¹⁰ is shown in Fig. 7-2. It consists of a valve, a connection to the bomb, and a steel hood over the inlet-gas tube to prevent mercury from entering this tube. This inlet tube projects into the open end of the piezometer. The ratio of the volume of the hood to the volume of the connecting tubing must be greater

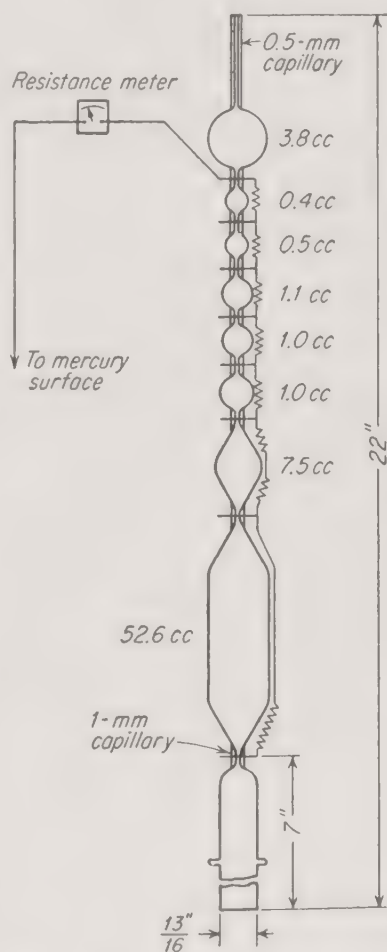


FIG. 7-1. Glass piezometer and platinum contact circuit. [From W. P. Hagenbach and E. W. Comings, *Ind. Eng. Chem.*, **45**: 606 (1953).]

¹⁰ W. P. Hagenbach and E. W. Comings, *Ind. Eng. Chem.*, **45**:606 (1953).

oscillations from an "antenna" placed adjacent to the thread of mercury to locate the position of the mercury. The strength of the signal changes greatly with the position of the mercury.

Mercury-cleaning Technique. Trace impurities in the mercury foul the platinum contacts so that the position of the mercury in the capillary tubes cannot be observed. Michels¹¹ suggests a procedure for cleaning mercury thoroughly.

The mercury is washed twice with benzene, followed by double washing in nitric acid, followed by double washing with water. After drying, the mercury is twice distilled in vacuo. This is followed by intensive washing in different liquids where the mercury is very finely dispersed in the washing liquid. [Figure 7-4] shows the arrangement. The mercury is poured into the porcelain tube *B*. This tube has a porous bottom, extending underneath the surface of the washing liquid. The surface tension of mercury is thus reduced so that the minute drops which come through the pores separate themselves from the porcelain. Those drops are so small that one can see them going up and down in the washing liquid. This method has two advantages. First, the time of contact between mercury and liquid is long. Secondly, the impurities in the mercury have only a short distance to travel to reach the surface of the droplets where they can go over into the washing liquid. The mercury drops collect at the bottom of the tube and siphon into a bottle. This procedure is applied four times with gasoline free of aromatics, twice with a mercurous nitrate solution, twice with nitric acid and six times with distilled water, after which the mercury is dried in vacuo. It is then once more filtered through a paper filter and again distilled in vacuo. The cooling tube of the still extends into the sampling bottle so that the mercury itself seals off the vacuum from the air. The mercury still is shown in [Fig. 7-5].

The mercury may also become contaminated by contact with materials used for valve packing and closure gaskets. A possible source is alumi-

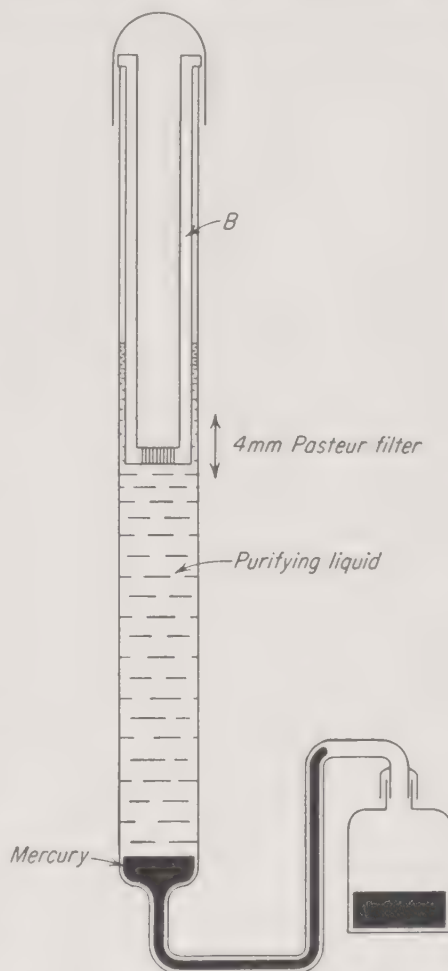


FIG. 7-4. Arrangement for washing mercury. (After A. Michels.)

¹¹ A. Michels, personal communication from the Van der Waals Laboratorium, Gemeente Universiteit, Amsterdam.

num. Mercury and aluminum normally do not react, but Maverick¹² found that this depends on the protection of a surface coating of aluminum oxide.

This is easily demonstrated with a strip of sheet aluminum. A drop of mercury is spread over the surface of the strip. When the oxide coating is abraded with sandpaper or a knife blade, trees of aluminum oxide will grow, forming a layer $\frac{1}{4}$ in. thick in 10 to 15 min. The surface of an aluminum gasket in contact with mercury may be scratched in making up the closure and lead to contamination of the mercury. Other mercury-cleaning techniques are described in Appendix G.

Constant-volume Method. This method was used below 1,000 atm at the Fixed Nitrogen Research Laboratory^{13,14,15} and by Townend and Bhatt,¹⁶ Holborn,¹⁷ Haney and Bliss,¹⁸ and Krichevskii and Markov.¹⁹ The apparatus used by Bennett and Dodge²⁰ at pressures up to 3,000 atm will be described. A schematic diagram of this apparatus is shown in Fig. 7-6. The constant-volume vessel was a coil of $\frac{1}{4}$ -in.-OD by $\frac{1}{16}$ -in.-ID chromium-molybdenum steel tubing 10 ft long with a volume of 6 ml. It was immersed in the constant-temperature bath

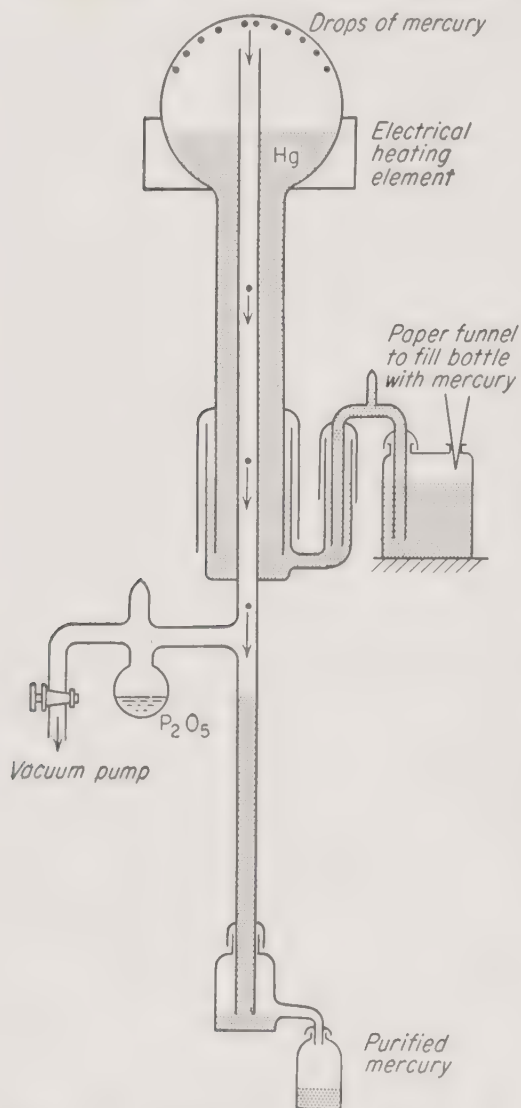


FIG. 7-5. Mercury still. (After A. Michels.)

K. The gas sample was compressed over water forced into the cylinder C

¹² A. L. Maverick, M.S. thesis, University of Illinois, Urbana, Ill., 1951.

¹³ E. P. Bartlett, *J. ACS*, **49**:687 (1927).

¹⁴ E. P. Bartlett, H. J. Cupples, and T. H. Tremearne, *J. ACS*, **50**:1275 (1928).

¹⁵ E. P. Bartlett, H. C. Hetherington, H. M. Kvalnes, and T. H. Tremearne, *J. ACS*, **52**:1363 (1930).

¹⁶ D. T. A. Townend and L. A. Bhatt, *Proc. Roy. Soc. (London)*, **134A**:502 (1931).

¹⁷ L. Holborn, *Ann. Physik*, **63**:674 (1920).

¹⁸ R. D. Haney and R. H. Bliss, *Ind. Eng. Chem.*, **36**:985 (1944).

¹⁹ I. R. Krichevskii and V. P. Markov, *Octo. Phys. U.R.S.S.*, **14**:271 (1941).

²⁰ C. O. Bennett and B. F. Dodge, *Ind. Eng. Chem.*, **44**:180 (1952).

by the intensifier *B* which was in turn operated by the hydraulic pump *A*. The gas pressure in the coil was measured by dead-weight gauge *F*. A suitable oil injector *H* and oil intensifier *G* operated the dead-weight gauge,

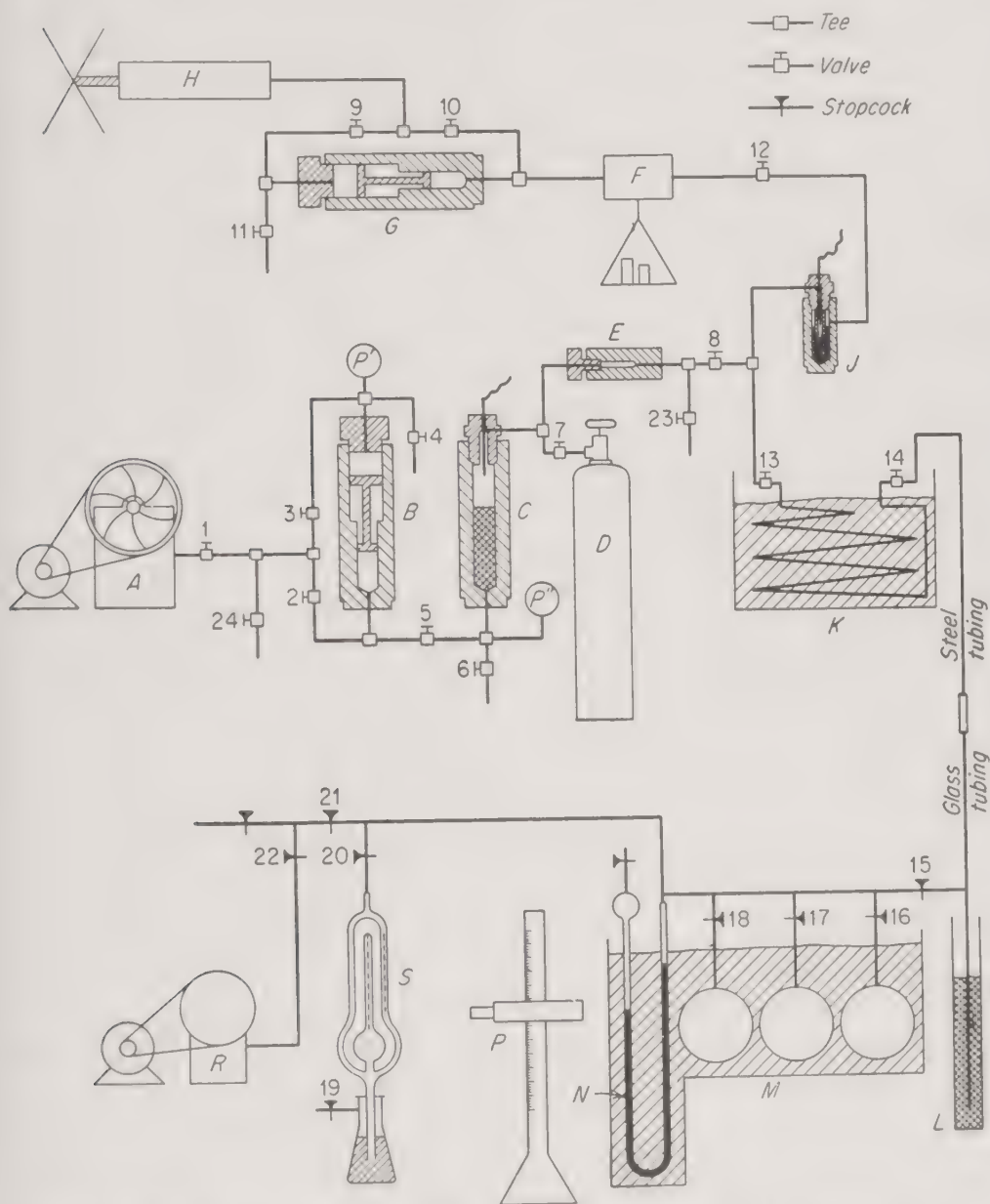


FIG. 7-6. Diagram of constant-volume apparatus. [From C. O. Bennett and B. F. Dodge, *Ind. Eng. Chem.*, **44**:180 (1952).]

and this oil system was isolated from the sample gas by the mercury U tube *J*. The quantity of gas in the coil between valves 13 and 14 was determined by expanding it to the three 2-liter glass bulbs held in the constant-temperature bath *M*. These had previously been evacuated by the vacuum pump *R* to a pressure of about 0.005 mm Hg.

The pressure before expansion was determined by the McLeod gauge S , and after expansion by the mercury manometer N with the aid of the cathetometer P . This latter pressure was in the range 500 to 1,200 mm Hg.

The gas-compression chamber C had an outside-to-inside-diameter ratio 3:1 with a 2-in. inside diameter. It was made of SAE 4140 steel, heat-treated to a yield point of 80,000 psi. According to the maximum-shear-stress theory, plastic flow should start at the inner diameter at a pressure of 35,000 psi. For purely plastic flow above the yield point, the plastic zone should reach the outside diameter at a pressure of 88,000 psi. The vessel was subjected to a preliminary hydraulic test of 60,000 psi so that a certain amount of plastic flow, or autofrettage, took place; thus the vessel should undergo no more plastic deformation under subsequent exposures to the maximum working pressure of 45,000 psi. The constant-volume coil was also given a preliminary autofrettage treatment at 60,000 psi and was subsequently held at 300°C for several hours to ensure elastic behavior.²¹

7-2. Phase Equilibrium. The designs of apparatus and techniques developed to observe the phase behavior under pressure of systems composed of one or more components make an extensive list.^{22,23} A few examples for observing gas-liquid phase equilibria will be described. Scheeline and Gilliland²⁴ clearly state the basis for two common methods and point out the features of each.

In the first method the mixture of hydrocarbons is introduced into a high-pressure bomb, which can be placed bodily in a thermostatically controlled bath of any desired temperature. The apparatus is equipped with a stirring or shaking device, vapor and liquid sampling lines, and temperature and pressure indicators. Agitation is continued until equilibrium between the phases is reached, at which time samples of liquid and vapor are withdrawn and analyzed. The method suffers from a number of drawbacks, which tend to complicate the apparatus. It is essential that two phases be present at equilibrium; therefore the correct amount of each component must be added to the bomb at the beginning of the run, and some level-indicating device is necessary. As critical conditions are approached and vapor and liquid properties become similar, it is difficult to control and measure the phase interface. In order to prevent pressure reduction and corresponding flashing of liquid when samples are withdrawn, it is necessary either to isolate the two phases in separate compartments of the bomb or to add an inert substance (usually mercury) as the sample is taken, which is equal in volume to the hydrocarbon removed. In order to ensure the attainment of

²¹ D. M. Newitt, "The Design of High Pressure Plant and Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.

²² P. W. Bridgman, *Revs. Mod. Phys.*, **18**(1):27-44 (1946).

²³ J. M. Smith, *Ind. Eng. Chem.*, **45**:963 (1953).

²⁴ H. W. Scheeline and E. R. Gilliland, *Ind. Eng. Chem.*, **31**:1050 (1939).

equilibrium, agitation must be prolonged and thorough, but provision must be made for preventing liquid droplets from entering the vapor sampling line.

The second method consists of obtaining the dew point and boiling point curves of a number of prepared samples of known composition. This can be done either by observing a break in a plot of temperature vs. pressure for a given sample, or by enclosing the sample in a thick-walled quartz tube in a thermostat and observing the pressure at which the first trace of vapor or liquid appears. By cross-plotting such dew- and boiling-point data, points are found at which saturated liquid and saturated vapor of different compositions exist at the same temperature and pressure; such points indicate phase equilibrium. One advantage of the method is that it conveniently gives valuable data on specific volumes; however, a number of serious drawbacks limit its general usefulness. The materials used must be carefully purified and free, in particular, from traces of fixed gases, for in the critical region the saturation pressure is quite sensitive to small amounts of air, etc. Furthermore, an extremely large amount of experimental work must be done in order to define completely and accurately the phase equilibrium over all values of concentration. But the most serious limitation of the method lies in the fact that it can be used only for systems of two components. In more complex systems it follows from the phase rule that composition is not a unique function of temperature and pressure, and that therefore dew and boiling point measurements alone cannot define the compositions of two phases in equilibrium.

Equilibrium Still. Scheeline and Gilliland describe their apparatus based on a third method which adapts the atmospheric-equilibrium still for use at elevated pressures. In this method a liquid is boiled in a still and the vapor is removed, without reflux, totally condensed, and continuously returned through a trap to the still body. Circulation is continued until equilibrium is reached, then the temperature and pressure are measured, and samples of liquid are withdrawn from the still and the condensate trap for analysis. Two problems to be met in using this method at elevated pressures are visual observation of the behavior in the still and the control of the pressure in the system. These were solved by constructing the still of glass and by controlling the heat input to the still by an automatic mercury switch operated as a pressure manometer. The assembly of the apparatus is shown in Fig. 7-7.

The still was composed of a 10-in. length of "Sonderglass" gage-glass tubing, 1 in. OD and $\frac{3}{4}$ in. ID, closed at one end. The top, or open end of the glass, was sealed by means of a packing gland such as is commonly used in gage-glass connections, the gasket being composed of a $\frac{1}{4}$ -in. layer of rubber and a $\frac{1}{4}$ -in. layer of "neoprene." The neoprene was in the upper position in contact with the hydrocarbon vapor. The bottom of the glass fitted into a depression in a steel base, the glass coming in contact with a padding layer of lead wool and another layer of rubber sheet. Three tie rods were provided from the lower piece of the packing gland extending through the base at the bottom.

The packing gland was machined from a piece of 2-in. steel hexagon. The four tubes entering the still were joined to the uppermost piece of the packing gland by silver solder. The four tubes were (a) the still sampling line, made of 0.057-in.-OD steel hypodermic tubing; (b) a thermocouple well made of $\frac{1}{4}$ -in.-OD copper tubing closed at the bottom; (c) the $\frac{5}{16}$ -in.-OD copper vapor exit line, the lower end of which was made flush with the inside of the steel piece; and

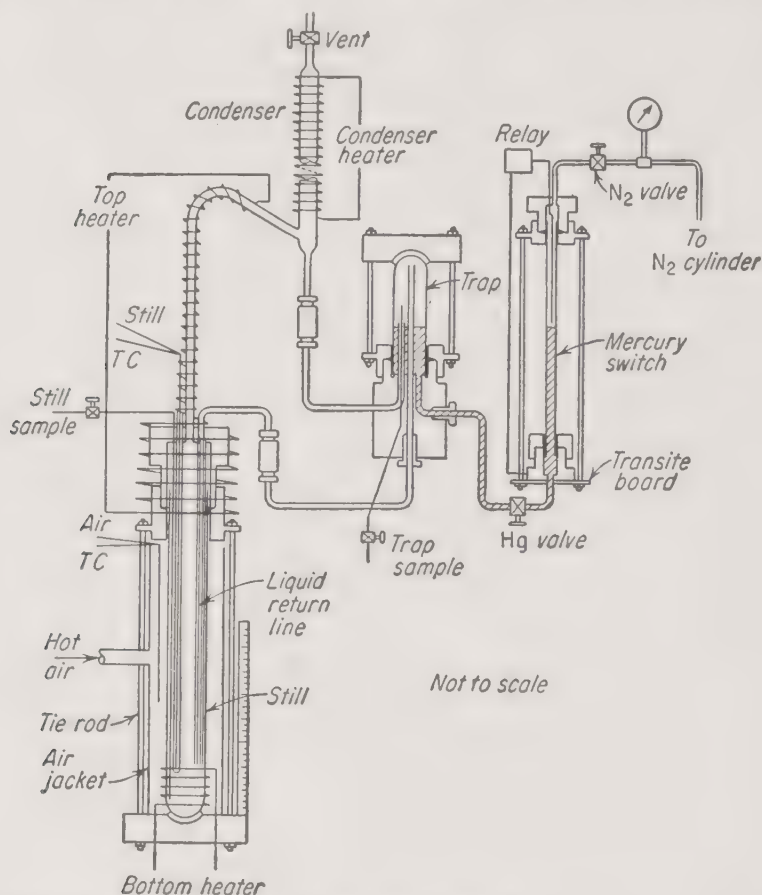


FIG. 7-7. Pressure-phase equilibrium still. [From H. W. Scheeline and E. R. Gilliland, *Ind. Eng. Chem.*, **31**:1050 (1939).]

(d) the liquid return line from the trap, made of $\frac{3}{16}$ -in.-OD seamless steel tubing with a 20-gage wall, which extended only half-way through the steel top. The lower part of the liquid return line, which formed the continuation of the one just mentioned, was made of two concentric copper tubes ($\frac{5}{16}$ and $\frac{3}{16}$ in. OD, respectively) with the annular space sealed with silver solder at the top, and with the inner tube provided with four small vent holes near the top to prevent siphoning of the liquid out of the trap. This concentric tube arrangement was used to prevent enrichment of the ascending vapors due to condensate formed on the liquid return line; the tubes were cemented into the steel top piece by means of "Sauereisen" porcelain cement. The sampling, thermocouple, and liquid return tubes all extended to within an inch of the bottom of the glass, and were arranged in such a way as not to touch the wall of the still.

In order to prevent reflux on the walls, the still was surrounded by a loosely fitting Pyrex glass jacket, into which a stream of hot air could be blown.

For the trap a 3¼-in. length of ¾-in.-OD × ½-in.-ID Sonderglass tubing was used, closed at the upper end. Packing gland, base, and tie rods were made similarly to those on the still, except in an inverted position. A ¼-in. thickness of rubber was used alone as the gasket, since it did not come in contact with the hydrocarbon. The lower part of the trap served as a mercury reservoir. Soldered connections could not be used in contact with mercury. The vertical tube for the influx of the condenser liquid was machined as an integral part of the main block. The other connections were made with steel compression cones.

The entire apparatus, except for valve stems, nitrogen line and cylinder, and pressure gage, was enclosed behind a safety booth made of ⅛-in. hardened steel sheet. Small holes were made in the booth for observation of the apparatus during operation; in all cases these holes were covered inside the booth by two thicknesses of safety glass.

Three heaters were used to control the temperature and pressure in the apparatus. The heaters were in series with variable resistances, so that heat input was at all times under close control. The current through the heaters could be varied independently through all ranges up to 10 amp. The bottom heater was a 1-ft length of No. 16 Chromel A wire encased in an asbestos sheath and coiled tightly around the bottom of the still. The top heater, 5 ft of No. 20 Chromel A covered similarly with asbestos, was coiled around the packing gland and the entire length of the vapor line. The condenser heater, 3 ft of No. 20 Chromel A wire sheathed in asbestos, was distributed over the entire length of the condenser.

The mercury switch controlled a 1-amp increment of current through the bottom heater (total current through this heater was generally from 5 to 8 amp). The mercury contact operated a small relay, which in turn controlled the heater current. The larger relay was of the type normally in the "on" position, so that the closing of the mercury contact reduced the heat input to the still.²⁴

Measurements were made at pressures up to 600 psi. Griswold and his co-workers^{25,26} have modified this type of apparatus and used it at temperatures up to 250°C and pressures of about 1,000 psi.

Dew-point and Boiling-point Apparatus. An apparatus for determining the dew-point and boiling-point curves for a multicomponent system is shown in Fig. 7-8 and is described by Kay and Rambosek²⁷ as follows:

A small sample of each of the mixtures was confined over mercury in the thick-walled glass capillary tube, 1, which was surrounded by the jacket, 2, and heated by the vapors of a series of organic liquids vaporized in the side-arm boiling flask, 9, by the electric heater, 17. The capillary tube was held in the compressor block, 4, which was connected to a manifold by copper tubing.

²⁵ J. Griswold, D. Andres, and V. A. Klein, *Trans. Am. Inst. Chem. Engrs.*, **39**:225 (1943).

²⁶ J. Griswold and S. Y. Wong, *Chem. Eng. Progr. Symposium Ser. 3*, **48**:18 (1952).

²⁷ W. B. Kay and G. M. Rambosek, *Ind. Eng. Chem.*, **45**:222 (1953).

Pressure adjustments were made through the manifold by the addition of high pressure gas from the cylinder, 5, or by releasing the gas through the exhaust valve, 18. The surge tank, 6, by increasing the volume of the system, served as a pressure stabilizer. Connected to the manifold were a pilot pressure gage, 7, to permit the pressure in the system to be adjusted quickly to the approximate value desired, and a dead-weight gage, 21, for the precise measurement of the pressure.

The latter was a commercial dead-weight gage tester modified by attaching an oil reservoir, 15. The pressure exerted by the gas on the oil was transmitted

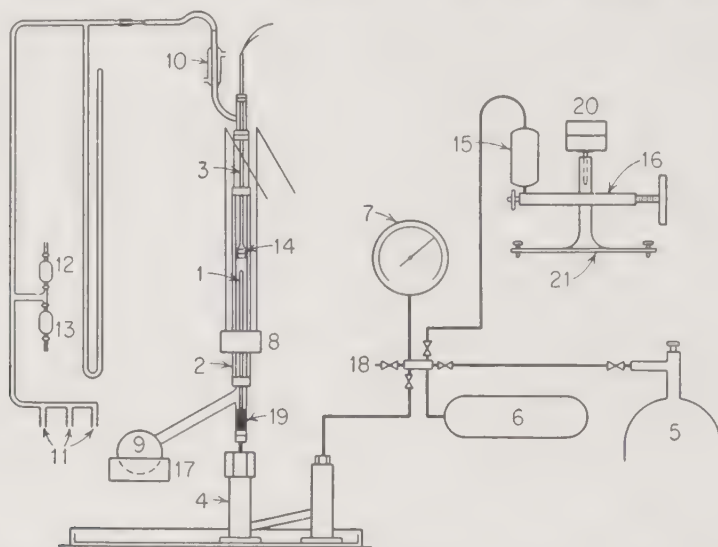


FIG. 7-8. Apparatus for pVT and phase-equilibrium measurements. [From W. B. Kay and G. M. Rambosek, *Ind. Eng. Chem.*, **45**:222 (1953).]

through the oil to the piston, 20. An 8-vaned air-driven spinner was installed on top of the pan to rotate the piston during measurements and minimize any lag or hysteresis due to friction between the piston and cylinder walls. When so rotated the piston was found to respond readily to a pressure change of 0.02 psi. The gage was calibrated against the vapor pressure of pure carbon dioxide at the ice point, as recommended by Bridgeman. The accuracy of the pressures measured with this gage is estimated to be better than 0.1 psi.

A handwheel moved a plunger, 16, in or out of the body of the gage. This plunger was used to vary the volume of the confined compressed gas by relatively small amounts, resulting in inverse changes in its pressure. The volume of the surge tank, 6, was such that one full turn of the handwheel changed the pressure in the system by about 0.002 psi.

The upper part of the jacket surrounding the experimental tube was attached through a side-arm condenser, 10, to three 5-gal bottles at point 11 and to a simple pressure regulating assembly, 12 and 13. A vacuum pump attached at 13 served to reduce the pressure over the boiling liquid in 9 to any desired value. Extremely small changes in pressure were made by evacuating bulb 13 or by filling bulb 12 with air at atmospheric pressure and then opening the appropriate stopcock to the line. The mercury layer, 19, prevented the boiling liquid from

coming in contact with the rubber stopper supporting the jacket. By the use of highly purified compounds and by close regulation of the pressure any temperature within a range of 50 to 70°, constant to within 0.02°F, was obtained with a single compound. The compounds used and their working temperature ranges were as follows: acetone, 100 to 132°; carbon tetrachloride 132 to 167°; chlorobenzene 167 to 270°F. For temperatures lower than 100°F, liquid from a constant temperature bath was circulated through an insulated jacket surrounding the tube.

The temperature of the vapor bath was measured by means of a copper-constantan thermocouple, 3, in conjunction with a sensitive potentiometer. The sensitivity was approximately 0.02°F. The couple was protected by a radiation shield and calibrated over the temperature range of the measurements by comparison with a platinum resistance thermometer which had been calibrated at the Bureau of Standards.

For the working section of the experimental tube, 1, a piece of precision bore glass capillary of about 2.1 mm bore was used. Its volume per millimeter was carefully determined so that the total volume of the sample at any temperature and pressure was obtained from a measurement of the length of the tube which the sample occupied.

The length was measured by means of a cathetometer reading to 0.05 mm. The accuracy of the volume measurements varied over a wide range, depending upon the length of the tube which a particular sample occupied. Expressed in terms of density, the uncertainty in the values was somewhere between 0.0015 g/cu cm for the liquid and 0.00015 g/cu cm for the vapor samples.

Equilibrium between the liquid and vapor phases of the sample in the tube was obtained quickly by moving a steel rod through the sample by means of an electromagnet, 8, around the outside of the heating jacket. The steel rod was enclosed in a tiny glass tube to eliminate the possibility of reaction with the iron.

[Figure 7-9] is a cross-sectional view of the compressor, showing its construction and the method of holding the experimental tube.

Gas pressure applied at the mercury surface in *B* was transmitted through the mercury to the sample in the tube. *D* was a safety check valve. The steel ball, *E*, owing to the difference in density of mercury and steel, normally floated at the top of the well and did not interfere with the normal flow of mercury. In the event that the tube burst under pressure, the sudden surge of mercury drove the ball into the valve seat, *F*, and prevented further loss of mercury.

The experimental tube was held in leg *A* of the compressor block in the following manner. An enlarged section or shoulder, *I*, was formed which rested on a small rubber cylinder, *H*, in the steel cup, *G*. The cup was constructed with a removable split ring bottom, *Q*, which was held in place by cap *R*. Sur-

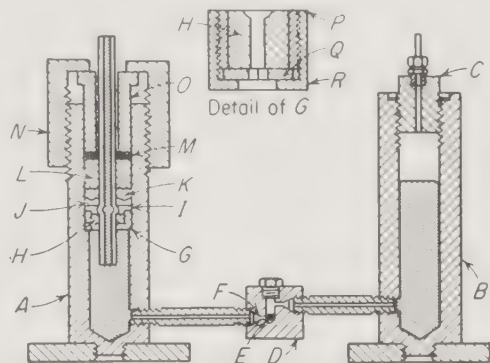


FIG. 7-9. Cross-sectional view of compressor. [From W. B. Kay and G. M. Rambosek, *Ind. Eng. Chem.*, **45**:222 (1953).]

rounding the tube above the shoulder were first a leather washer, *J*, then a loose-fitting steel washer, *K*, with a machined bottom face to form a bearing surface for the shoulder, the rubber cylinder, *L*, which effected the stuffing box seal, a thin steel washer, *M*, gland, *N*, and finally, the cap, *O*, which, when drawn down, compressed the rubber cylinder, thus making the seal. The tube so prepared, when fitted into *A*, rested on a shoulder therein. To facilitate removal and installation of the assembly, the diameter of the rubber cylinder and the leather washer were made $\frac{1}{16}$ in. less than the inside diameter of leg *A*.

The sample to be tested was prepared and sealed in special glass bulbs with a U-shaped tip. This tip was submerged in mercury and inserted under a glass collecting tube filled with mercury. When the tip was broken, part of the sample was transferred to the collecting tube. From here the sample was taken up in a microburet. After measuring its volume, temperature, and pressure, it was transferred under mercury to the experimental tube. Measurements are reported at pressures up to 1,200 psi.

Phase-volume Apparatus. The apparatus described by Sage and Lacey²⁸ permits the measurement of the equilibrium volume of liquid and vapor phases formed from a mixture of known composition. The cell has a working range of temperature from 0 to 460°F at pressures up to 10,000 psi. The equilibrium cell *A* is shown in Fig. 7-10. This is immersed in the constant-temperature bath *U*. The components of the mixture to be tested are admitted through the valves *I* and *J*. The mixture is agitated by the spiral agitator *V* to attain equilibrium. This occupies the same cross section of the cell at all levels except near the top and bottom. This agitator is connected to an armature which is rotated by electromagnets acting through the stainless-steel wall which confines the armature.

Mercury is forced into the cell from below and confines the sample to the remaining volume of the cell. The armature operates submerged in the mercury. The head *E* is fitted with a single and double point on its lower face. The mercury surface is located by contact with the single point using a suitable electric circuit. The liquid-phase surface is located by the double point. A length of platinum wire is spark-welded to these two points, and a small current is passed through the wire. The slight difference in the rate of heat dissipation from the wire in vapor and liquid locates the interface. Other features of the design include:

- a. A compensation rod to adjust for the change in volume as *E* moves up or down
- b. A worm-driven nut which operates the level indicator *E*

²⁸ B. H. Sage and W. N. Lacey, *Am. Inst. Mining Met. Engrs. Tech. Publ.* 2269 (1947).

c. An unsupported-area closure at D' designed for minimum change in volume of the cell

d. An oil-balanced packing gland around the level-indicator rod which prevents the leakage of mercury

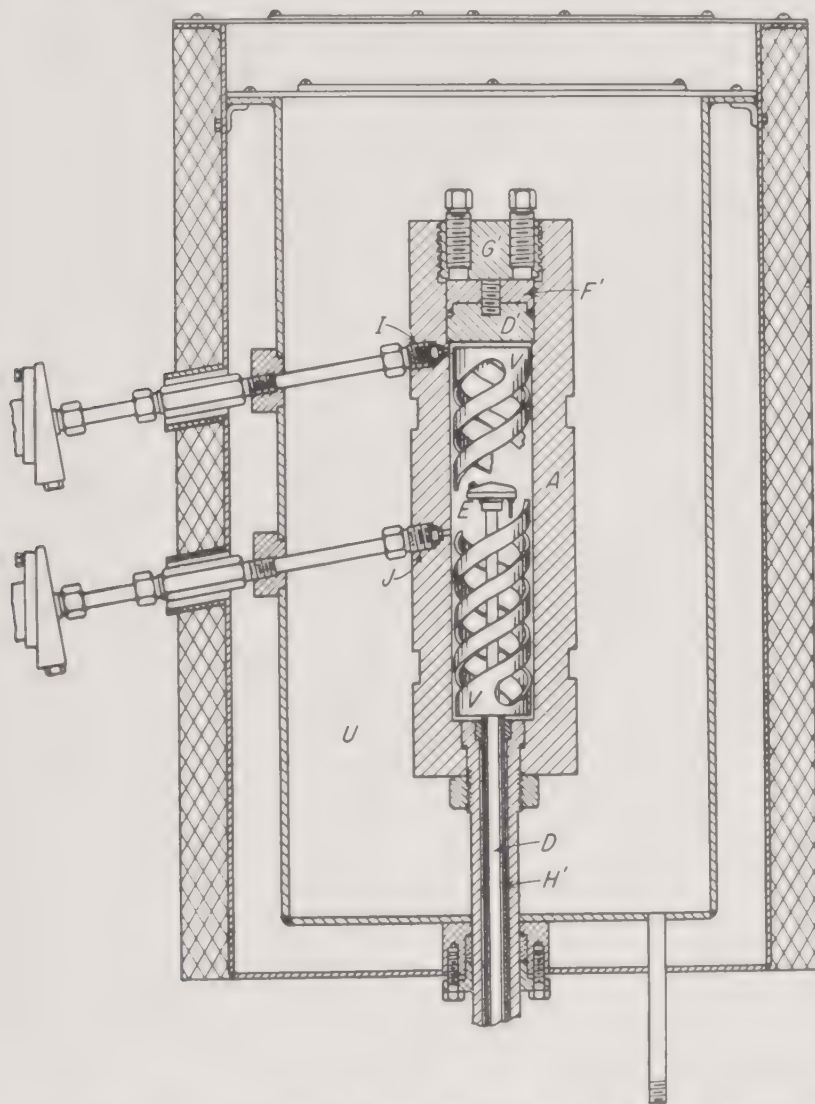


FIG. 7-10. Equilibrium cell. [From B. H. Sage and W. N. Lacey, *Am. Inst. Mining Met. Engrs. Tech. Publ.* 2269 (1947).]

After thermal and phase equilibrium are attained at one state of the system pressure, temperature and volume readings are taken.

Vapor-liquid Equilibrium above 10,000 psi. The critical pressure of pure substances is normally less than 1,500 psi, and vapor and liquid do not exist as separate phases above this pressure for most pure substance. Water is an exception, with a critical pressure of 3,206 psi. When the

critical temperatures of substances in a mixture differ widely, such mixtures display critical pressures much higher than for a pure substance. Rzasz and Katz²⁹ have demonstrated the coexistence of liquid and vapor phases at pressures of 25,000 psi in mixtures of methane and Kensol (a narrow-boiling-range oil with an experimentally determined average molecular weight of 246.9). The measurements were made in a high-pressure cell containing 10 windows which could be used for visual observation of the phase phenomena. Opalescence was observed in the

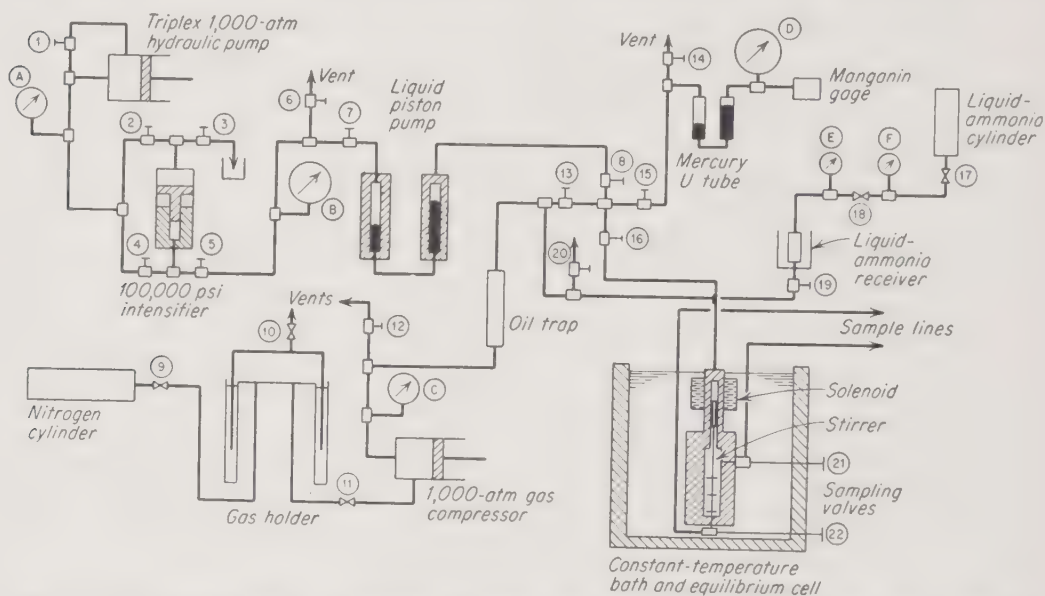


FIG. 7-11. Apparatus for phase equilibrium at pressures up to 3,750 atm. [From A. E. Lindroos and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **48**(3):10 (1952).]

region of the critical point in all mixtures with composition between 45 and 55 weight per cent methane. The mixtures appeared cherry red to brown red by transmitted light and blue green by reflected light. Critical opalescence is believed to be caused by the association of molecules into tiny droplets of the liquid phase or bubbles of the vapor phase. The color phenomena were definitely discernible over the entire range of temperatures investigated, with temperatures differing from the critical temperature by as much as 100°F or more.

Measurements are reported by Lindroos and Dodge³⁰ on the coexistence of two phases in the system nitrogen-ammonia at pressures to 3,750 atm. Figure 7-11 is a diagram of the apparatus used. Ammonia was introduced into the equilibrium cell as a liquid at its vapor pressure. Nitrogen was compressed by a Norwalk gas compressor to 1,000 atm and introduced into the equilibrium cell and into the right leg of the

²⁹ M. J. Rzasz and D. L. Katz, *Petroleum, Trans. ASME*, **189**:119 (1950).

³⁰ A. E. Lindroos and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **48** (3):10 (1952).

mercury liquid-piston pump. To increase the pressure beyond 1,000 atm, the nitrogen in the liquid-piston pump was forced into the equilibrium cell by means of an intensifier which acted on the liquid piston. By repeatedly filling the liquid-piston pump to 1,000 atm with nitrogen and actuating the mercury piston, the pressure in the equilibrium cell was increased to any desired value. After allowing time for the contents of the cell to reach the temperature of the oil bath in which the cell was totally immersed, a magnetic stirrer within the cell was put in operation. After 3 hr of intermittent agitation, the pressure within the equilibrium cell was measured by a manganin resistance gauge, and samples of each phase were taken and analyzed. The pressure after sampling was also taken to determine the pressure drop during sampling. These authors cite investigations by others of two-phase behavior in this system to a pressure of 9,700 atm.

7-3. Heat Capacity. The heat capacity of gases increases appreciably with increase in pressure. The increase above atmospheric pressure may be measured, or it may be calculated from measurements of the Joule-Thomson coefficient or from pVT measurements. The calculation from pVT measurements is apparently the preferred method. Precise measurements are necessary since the calculation requires the evaluation of a second derivative, and the precision of the calculated results is considerably less than of the original data. In the region near the critical, the second derivative is seldom known with sufficient accuracy to permit calculation of the heat capacity.

Unsteady-state, Nonflow Method. Measurements of the heat capacity of carbon dioxide over a considerable range including the critical are described by Michels and Strijland.³¹ Quoting from these authors:

Consideration of the factors, limiting the precision of C_V measurements, leads to three main requirements to be fulfilled.

1. In the critical region the heat capacity of a fluid varies rapidly with temperature. Each measurement gives an average value over a certain temperature interval. Therefore these intervals should be as small as possible.

2. The heat capacity of a high pressure gas container is many times larger than the heat capacity of the gas itself. This larger quantity must be eliminated by employing a differential method.

3. To minimize thermal losses the use of an adiabatic calorimeter is essential viz. the calorimeter should either have no thermal contact with the surroundings or should be permanently in thermal equilibrium with its surroundings.

In the present work it was tried to adhere closely to those principles.

Two identical calorimeters were used, one filled with the substance under investigation and the other evacuated. Each calorimeter carries a winding of platinum wire, serving alternately as thermometer and as heater.

³¹ A. Michels and J. Strijland, *Physica*, **18**:613 (1952).

The experiment consists essentially of three different stages.

a. During the first stage calorimeters and surroundings are at the same constant temperature. This temperature is calculated from the resistance of the platinum coils.

b. During the second stage the calorimeters are heated by an electric current through the coils, which are now connected in series. The temperature of the surroundings is made to follow automatically the temperature of the calorimeters.

c. The third stage begins when the heating is stopped. Again the temperature is obtained from resistance measurements. The small temperature difference which exists between the two calorimeters, mainly resulting from the difference in heat capacity of the two systems, is determined.

[Figure 7-12] shows a cross section of the assembled calorimeters. Two silver tubes *C* are screwed through the bottom of the brass cylinder *B*. The tops of these tubes carry porcelain discs *E* from which are hung the calorimeters *I* and *II* by means of strong silk threads *F*. The seal between *E* and *C* is vacuum-tight. The tube *D* leads to the evacuation system. The outer walls of the calorimeters and the inner walls of *C* are polished. Around each calorimeter two coaxial cylinders *G*, made of aluminum foil, are placed. Thus heat transfer by conduction, convection or radiation is reduced to a permissible minimum.

The calorimeters each consist of two separate parts: a steel container and a heating element of platinum wire encased in a brass sheath.

A small opening in the top of the steel container is closed by a valve. During evacuation and filling of the bomb this spindle has to be packed. Therefore a detachable part is provided, which, together with the connecting piece, is removed before the measurements.

The temperatures of the calorimeters are derived from the resistances of the two platinum coils R_I and R_{II} , and the final result depends on the difference in temperature between the two calorimeters at the end of the

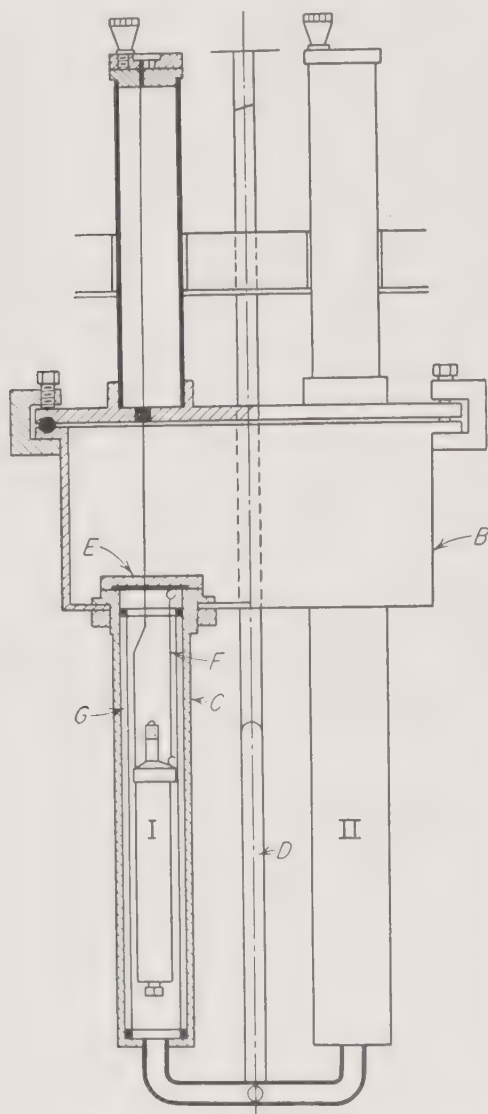


FIG. 7-12. Heat-capacity apparatus. [From A. Michels and J. Strijland, *Physica*, **18**:613 (1952).]

run. This difference must be corrected for heat losses to the oil bath. During the run, temperatures of the two calorimeters and the oil bath are not the same, since both the heat input to the calorimeters and the heat capacity of the calorimeters are slightly different. The oil bath automatically follows the mean temperature of the two.

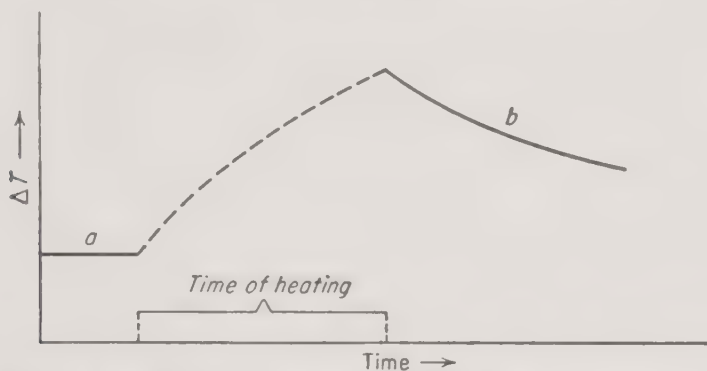


FIG. 7-13. Variation in temperature difference between the two calorimeters during the run. [From A. Michels and J. Strijland, *Physica*, **18**:613 (1952).]

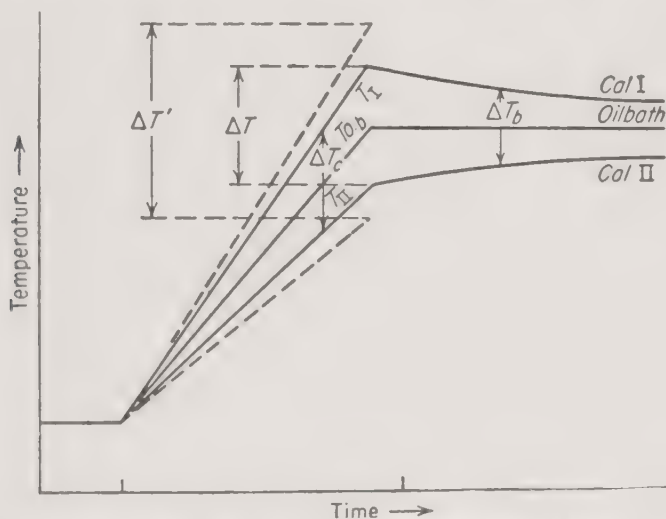


FIG. 7-14. Temperatures of the two calorimeters and the oil bath. [From A. Michels and J. Strijland, *Physica*, **18**:613 (1952).]

The difference in temperature between the two calorimeters varies during the run as shown in Fig. 7-13. The temperatures of the two calorimeters and the oil bath are shown in Fig. 7-14. The measured temperature difference ΔT is corrected to give the temperature difference $\Delta T'$ which would be measured if there were no heat losses during the run. The volume of the steel container is measured, and the quantity of test gas is determined by weighing. The energy is determined from the electric input. From these measurements, the specific heat is determined

to fourth-place accuracy as the mean value for the temperature interval involved and at a known density. These intervals were of the order of 1 to 1.5°C.

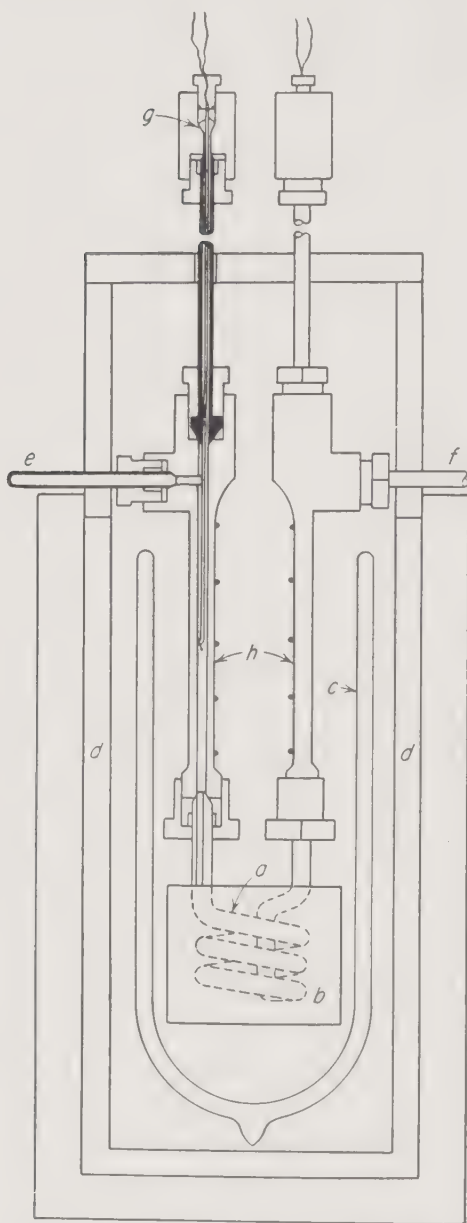


FIG. 7-15. Flow calorimeter. [From N. W. Krase and B. H. Mackey, *J. ACS*, **52**:108, 5111 (1930).]

Steady-state-flow Method. The method used by Krase and Mackey³² is an example of the measurement of the specific heat of gases by a flow method at pressures up to 700 atm and temperatures to 150°C. A compressed gas was passed through the apparatus at a steady rate which ranged from 0.7 to 1.5 moles/min in separate experiments. This rate was regulated by a hand-controlled valve which was heated to counteract the cooling due to expansion. The gas then passed through a thermostat, a calorimeter, an expansion valve, an indicating capillary flow-meter, a humidifier, and a wet-test meter. The thermostat was a coil of steel tubing with a copper block cast around it. An electric heater was wound on the casting, and a Beckmann thermometer was placed in a hole in the casting. The temperature was controlled manually to about 0.01°C. The gas was pre-heated in the thermostat to a temperature 5 or 6°C below the calorimeter temperature.

The flow-type calorimeter is shown in Fig. 7-15. It consists of a coil of steel tubing *a* embedded in a copper casting *b* and placed in a Dewar flask *c*. The copper casting contains an electric resistance heater and a thermometer. To further reduce heat losses, the Dewar flask is

surrounded by a heavy cylindrical copper casting *d* closed at both ends with copper disks. This copper jacket is kept at the same temperature as the calorimeter by a noninductive resistance winding. The gas enters through

³² N. W. Krase and B. H. Mackey, *J. ACS*, **52**:108, 5111 (1930).

the horizontal tube *e* at the left, passes down the vertical tube, through the coil, up the right-hand tube and out the horizontal tube at the right *f*. During its passage, it takes up heat from the calorimeter, and its temperature rises to within about 0.06°C of the temperature of the calorimeter. The wires for the thermocouples, reading the inlet and outlet temperatures of the flowing gas, pass through fittings at the top ends of the vertical steel tubes. These fittings may be removed for calibration of the thermocouples without disturbing the Bakelite seals *g* around the wires or other connections. The fittings are about 13 cm above the calorimeter cover, and the Bakelite compression seals are at a lower temperature than the calorimeter. These tubes are long enough so that the temperature gradient decreases along the portions of the tube through which the gas flows. This reduces the conduction of heat along the tube walls and also along the thermocouple wires. A correction for the conduction along the tube walls is determined by "gradient" tubes *h* having a uniform steel cross section for a length of 10 cm. Five thermocouples are equally spaced along each of these gradient tubes and serve to determine the temperature drop along the tubes. This permits a calculation of the heat conducted out of the calorimeter block. Other corrections were made for some inductive heating of the calorimeter by the jacket winding, and for the temperature change due to the Joule-Thomson effect resulting from the pressure drop within the calorimeter. The capillary flowmeter, humidifier, and wet-test meter were enclosed in a constant-temperature compartment. Small changes in temperature were sufficient to alter the calibration of the wet-test meter considerably. The specific heat was calculated from the gas-temperature rise, the molal flow rate, and the energy input.

7-4. Viscosity of Gases. The determination of viscosity requires the measurement of a force per unit area or shearing stress and the velocity or velocity gradient resulting from this force in a fluid moving in laminar flow. When measuring the viscosity of gases under elevated pressures, difficulty has been encountered with some types of viscometers in avoiding turbulent conditions. This is due to the ease with which the critical Reynolds number is exceeded because of the rapid decrease of the ratio of viscosity to density with increasing pressure. When turbulence occurs, a form drag is effective in addition to the viscous drag, and inertial forces then come into play. Although any viscometer can be calibrated for use under turbulent conditions, the accuracy is then less satisfactory. An ideal viscometer would be one in which the inertia effects are negligible and the observed results are due entirely to the viscous drag.

A method involving the measurement of the rate of damping of an oscillating disk was first used by Maxwell. The disk was suspended by a wire connected at its center so that it rotated freely between two other

parallel, stationary disks. The viscosity is related to the rate of damping of the oscillations. This type of instrument is more suitable for relative measurements than for direct determinations of viscosity. It should be calibrated with a gas of known viscosity. If gases at atmospheric pressure are used to calibrate the instrument, the calibration may not be valid at the higher pressures if turbulence is encountered. When using an instrument of this type, it is advisable to look for evidence of turbulence. One method of doing this is to repeat the determination using different spacings between the disks. If the results are the same, the turbulence is negligible. The theory of an oscillating-disk viscometer has been improved upon by Mason, Naldreth, and Maas,^{33,34} who used this type to determine the viscosity of ethylene and carbon dioxide near the critical densities. Their measurements are of high precision and are in good agreement with those of other investigators. This indicates that turbulence was not encountered in the pressure range they used.

A rotating-cylinder-type viscometer has been used at low pressures. This consists of two coaxial cylinders with the fluid between them. The viscosity can be calculated from measurements of the drag when one cylinder is rotated with respect to the other. As with the oscillating-disk viscometer, the accuracy of the results depends upon maintaining laminar conditions. This type of apparatus has not been successfully used for measurements at high pressures.

A falling-body-type instrument has been used for measurements on gases at high pressures. This viscometer consists of a cylindrical body which falls freely in a closely fitting vertical tube. The fluid is transpired through the annular space, creating a viscous drag on the falling body. Along with this viscous drag, there are additional drags due to the fluid displacement at the front of the falling body, the establishment of the velocity gradient in the annular space, and the turbulent wake in back. In calculating the viscosity from the fall-time data, the end effects are neglected. If laminar conditions are maintained in the annular space, the results should be fairly accurate, provided the end effects are small in comparison to the viscous drag.

The rolling-ball-type instrument was first proposed by Hersey³⁵ and later modified by Sage³⁶ for use at high pressures. This instrument consists of a ball which rolls freely through an inclined, closely fitting tube. Since the hydrodynamics of the flow are complicated, the instrument is suitable for relative measurements only. It was found by Sage and his co-workers that turbulent conditions could not be avoided over the whole

³³ S. G. Mason and O. Maas, *Can. J. Research*, **18B**:128 (1940).

³⁴ S. N. Naldreth and O. Maas, *Can. J. Research*, **18B**:322 (1940).

³⁵ M. D. Hersey, *J. Wash. Acad. Sci.*, **6**:525 (1916).

³⁶ B. H. Sage, *Ind. Eng. Chem. Anal. Ed.*, **5**:261 (1933).

pressure range with gases. Hence, this instrument has to be calibrated for turbulent as well as for laminar conditions.

The method of transpiration through a capillary tube has been used in many modified forms. The method consists of applying Poiseuille's law to laminar flow through straight tubing of circular cross section. Since the theory of laminar flow in a tube is well established, the capillary method is the most reliable for direct determinations. One difficulty with this method is the accurate determination of the small pressure drop for the low rates of flow necessary to maintain laminar conditions. The Rankine viscometer³⁷ overcomes this difficulty and is capable of high accuracy. For direct determinations of viscosity the diameter must be known accurately since the diameter is raised to the fourth power in Poiseuille's equation. If the capillary is long relative to its diameter, the end effects will be small; however, they should either be shown to be negligible or else be taken into account in the calculations.

The Rankine viscometer used by Comings, Mayland, and Egly³⁸ will be described. This was a glass viscometer enclosed in a steel pressure vessel. Nitrogen gas was maintained in the steel vessel under the same pressure as that of the gas sample inside the glass instrument. The glass viscometer is shown in Fig. 7-16. The viscometer assembled inside the pressure vessel is shown in Fig. 7-17. The glass viscometer consisted of two parallel Pyrex-glass tubes joined at both ends. One tube is a heavy-walled capillary, and the other is a standard thin-walled tube. The capillary tube is long relative to its diameter, so that end effects are minimized. A mercury pellet in the larger tube exerts a pistonlike action and forces the gas through the capillary. The weight of the pellet furnishes the pressure difference across the capillary. By carefully choosing the size of the capillary tube and the mass of the mercury pellet, laminar flow through the capillary can always be assured. Two tungsten wires were carefully sealed in the wall of the larger tube near the top in such a way as to cause very little distortion of the tube diameter. Two similar wires were placed near the other end of the tube, and each of these pairs were used to indicate the passage of the mercury pellet. When the pellet closed the circuit through a pair of these wires, a current of a few milliamperes signaled its passage. The time of fall of the mercury pellet between the two pairs of wires was measured.

The technique³⁹ developed for inserting the tungsten wires consisted of first coating the wire with glass and then inserting an uncoated tip of the wire through the wall of the partially preheated tube. Tungsten will

³⁷ A. O. Rankine, *Proc. Roy. Soc. (London)*, **83A**:265 (1912).

³⁸ E. W. Comings, B. J. Mayland, and R. S. Egly, *The Viscosity of Gases at High Pressures*, *Univ. Illinois Eng. Expt. Sta. Bull.* 354 (1944).

³⁹ R. S. Egly, Ph.D. thesis, p. 106, University of Illinois, 1940.

make an excellent seal with glass if the tungsten is coated with a very thin layer of tungsten oxide; and the tungsten oxide reacts with the Pyrex glass to form a gold-colored compound. The tungsten wire is first degasified by heating in an oxygen-gas flame to white heat. Then segments an

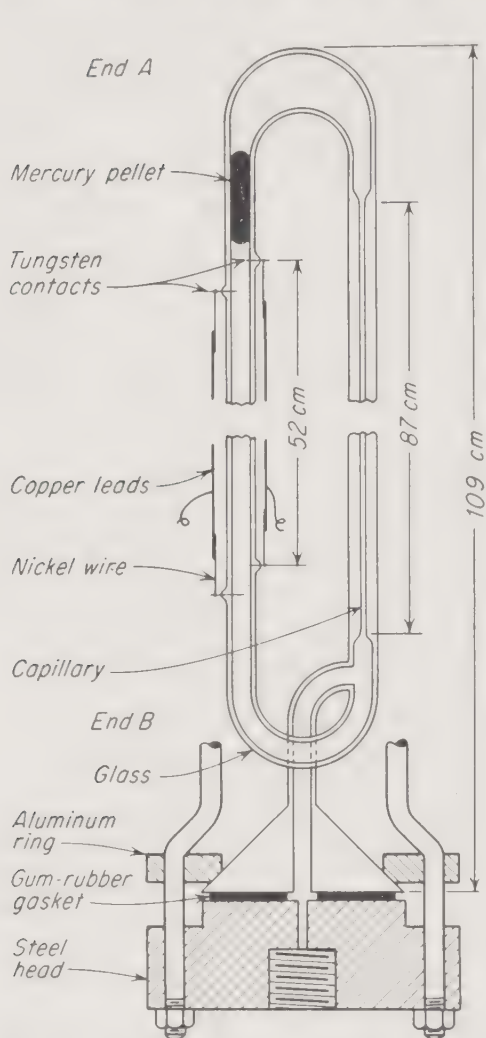


FIG. 7-16. Glass viscometer. [From E. W. Comings, B. J. Mayland, and R. S. Egly, Univ. Illinois Eng. Expt. Sta. Bull. 354 (1944).]

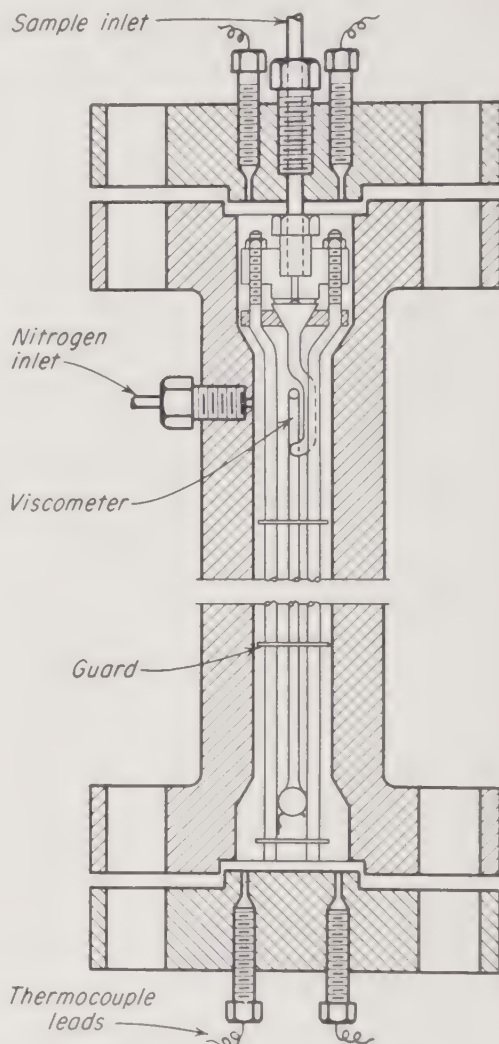


FIG. 7-17. Viscometer assembled in bomb. [From E. W. Comings, B. J. Mayland, and R. S. Egly, Univ. Illinois Eng. Expt. Sta. Bull. 354 (1944).]

inch or two long are placed in the chuck of an electric drill and rotated against emery paper to polish the wires and remove any surface coatings. The tungsten wires are next covered with a thin film of oxide by heating them in an oxidizing flame. Then a piece of Pyrex tubing is drawn out until it is just large enough to slip easily over the tungsten wire. A piece of this tubing about 1 cm long is slipped over the wire leaving about 1 mm of the wire protruding, and the glass and wire are heated. It is a simple

matter to tell when the Pyrex and tungsten have been sealed together because of the formation of the gold-colored compound. A small hole is then drilled through the tube wall by means of a tungsten wire heated to white heat. The tungsten wire coated with the glass bead is inserted through this hole, and the bead and the tube wall are carefully fused together with a tiny oxygen-hydrogen flame. During this process, the inside wall of the tube around the wire tends to become coated with a gray film, presumably tungsten oxide, and excessive heating of the tube wall must be avoided in order to prevent this oxide from uniting with the tube wall. Both this gray film and the oxide layer on the portion of the contact projecting within the tube may be removed by running molten sodium nitrate through the tube. Tungsten contacts can be sealed into the tube in this manner with practically no disturbance of the cross section.

Modifications have been made in this type of viscometer by N. L. Carr.⁴⁰ The time of fall of the mercury pellet was measured by an electronic instrument. Rings were fastened to the fall tube in the desired positions, and these were connected to a sensitive capacity-detecting instrument.⁴¹ The fall tubes were made of precision-bore Pyrex tubing (obtained from the Fischer-Porter Company), and the apparatus was designed for pressures up to 15,000 psi.

The temperature of the University of Illinois bomb³⁸ was controlled by wrapping it with a single main resistance wire augmented by three control coils equally spaced over each third of the length. Each head was also insulated by a hood provided with a main and a control heater winding. The temperature was held constant by an automatic temperature controller to $\pm 0.5^{\circ}\text{C}$, and this was improved by manual adjustment during the test period so that the variation was seldom more than $\pm 0.3^{\circ}\text{C}$.

The entire bomb was pivoted about its mid-point to permit its rotation through 180° . This allowed the viscometer to be inverted in order to repeat the measurements in each direction. The sample line and the nitrogen line were joined to the rest of the system through coils of small-diameter flexible tubing; thus it was unnecessary to break any connections when the bomb was rotated. Lines carrying the test sample were electrically heated to prevent condensation at the elevated pressures.

For application to these measurements, Poiseuille's law may be written in the form

$$\Delta p_c = - \frac{8\nu\mu}{\pi t} \int_0^L \frac{dL}{r^4} \quad (7-1)$$

⁴⁰ N. L. Carr, Viscosity of Natural Gas Components and Mixtures, *Inst. Gas Technol. Research Bull.* 23 (1953).

⁴¹ R. H. Müller, *Ind. Eng. Chem. Anal. Ed.* **19**(10):21A (1947); thermocap relay manufactured by Niagara Electron Laboratories, Andover, N.Y.

where Δp_c = pressure drop in the capillary
 v = volume displaced by the pellet
 μ = viscosity
 t = time of fall of pellet
 L = length of capillary
 r = radius of capillary

This applies rigorously when the rate of flow is constant. For an incompressible fluid and a viscometer with an unsymmetrical distribution of gas

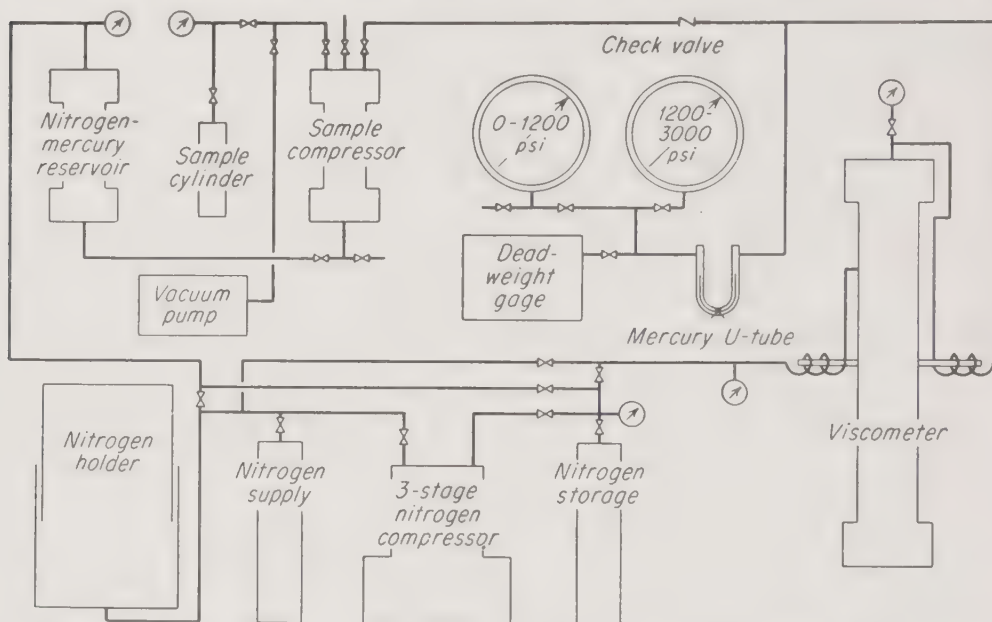


FIG. 7-18. Flow diagram of viscosity apparatus. [From E. W. Comings, B. J. Mayland, and R. S. Egly, *Univ. Illinois Eng. Expt. Sta. Bull.* 354 (1944).]

volume above and below the pellet, the rate of flow changes by a small amount during the passage of the pellet. The error from this is less than 0.01 per cent if the time of fall is taken as the average of an equal number of readings with the bomb upright and inverted, respectively. A correction is applied for the effect of capillarity on the mercury pellet. The integral $\int_0^L (1/r^4) dL$ is evaluated by measuring the length of a small thread of mercury at a number of positions along the capillary using a horizontal cathetometer.

A flow diagram of the complete apparatus is shown in Fig. 7-18. The pressure in the viscometer was measured by two Bourdon-type pressure gauges, 12 in. in diameter, one of which covered the range from 0 to 1,200 psi and the other that from 1,200 to 3,000 psi. These gauges were filled with oil and were compared with a dead-weight gauge at frequent intervals. The test sample was compressed to the desired pressure over mercury in the sample compressor. Mercury was forced into this cylinder

from a second cylinder by nitrogen under pressure. The nitrogen for the latter cylinder and for the viscometer bomb was compressed by a three-stage Rix compressor.

To operate the system, the mercury pellet was held in the enlarged end *A* of the viscometer with this end down. In this position it did not interfere with the flow of gas. The pressure and temperature were adjusted and allowed to stabilize. The fall time of the pellet between the tungsten wires was then observed from 2 to 7 times in each direction. The maximum deviation from the average time of fall was less than 0.5 per cent. The viscosity was determined from the average time of fall of the mercury pellet, the calibration constant of the pellet, and the known dimensions of the instrument.

7-5. Thermal Conductivity. The thermal conductivity of gases has been measured at atmospheric pressure by a number of investigators using modifications of the "hot-wire" method originally employed by Schleiermacher.⁴² This method makes use of a wire stretched axially in a tube with the test gas surrounding the wire. The wire serves both as an electric heater and also as a resistance thermometer. The thermal conductivity is the constant k in the equation

$$\frac{q_c}{A} = k \frac{dt}{dy}$$

where q_c = rate of heat transfer by conduction only

A = area normal to the direction of heat flow

dt/dy = temperature gradient in the direction of heat flow

The direct measurement of k consists in measuring the rate of heat transfer by conduction per unit area q_c/A , the temperature difference across a thin gas layer, and the thickness of the gas layer. The evaluation of q_c/A requires the elimination, or a correction for the loss, of heat which does not pass through the gas layer and also for heat which passes through the gas layer by radiation and by convection. The elimination of convection has been the most troublesome, since there is an increasing tendency for natural convection to occur as the pressure is increased. This tendency is infinite at the critical temperature and pressure and then decreases at higher pressures.

The tendency for natural convection may be reduced (*a*) by avoiding temperature gradients that result in increase in density with increase in vertical distance, and (*b*) by using thin gas layers so that the drag of the bounding surfaces eliminates the convection currents. The construction of a hot-wire apparatus involves insurmountable difficulties at high pressures, and this has led to the use of other designs. Different designs

⁴² A. Schleiermacher, *Ann. Physik*, **36**:346 (1889).

permit either direct measurement or indirect measurement by comparison with a gas of known thermal conductivity.

Direct Methods. The apparatus described by Michels and Botzen⁴³ permits measurement at pressures up to 3,000 atm with an accuracy of about 1 per cent. This consists of two horizontal, parallel plates with the upper plate held at a slightly higher temperature. The gas sample is between the plates. The density tends to decrease with increase in the

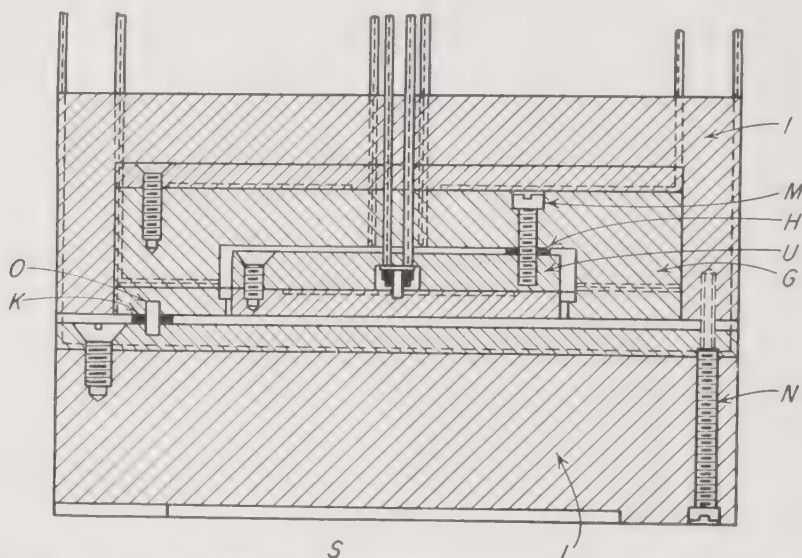


Fig. 7-19. Parallel-plate type of thermal-conductivity cell. [From A. Michels and A. Botzen, *Physica*, **18**:605 (1952).]

vertical distance above the lower plate, and this suppresses natural-convection currents. The method also provides a uniform temperature gradient through the gas layer, rather than a variable gradient as in the methods in which the test gas is in an annulus. The description provided by these investigators is quoted below:

The thermal conductivity cell is shown separately in [Fig. 7-19]. *U* is the upper and *L* is the lower plate, the latter being in good thermal contact with the bottom of a heavy walled steel vessel *S* placed in a thermostated oil bath. Each plate consists of two copper discs enclosing platinum wires. These wires are embedded in a spiral groove; they serve simultaneously both as heaters and resistance thermometers. The wires are 0.1 mm thick and insulated by 0.5-mm-OD polythene tubing. As the gas can enter the space between the discs, the danger that the plates could be deformed under high pressure is avoided. A copper guard ring *G*, in which a platinum wire is also embedded for heating purposes, envelops the upper plate. It is kept at a distance of 1.4 mm by three small glass spacers *H*. The upper plate and the guard plate are screwed together by teflon bolts *M* passing through holes drilled in these spacers. Teflon is also used for the insulating cap *I* surrounding *G*. After assembling the upper unit,

⁴³ A. Michels and A. Botzen, *Physica*, **18**:605 (1952).

its lower surface is machined optically flat. The surface of the lower plate *L*, facing the top plate, is also made optically flat. The relative position of the upper and the lower part of the conductivity cell is guaranteed by small glass spacers *K*, the teflon rods *O* and the teflon bolts *N*. Glass spacers were available in sizes of 1, 1½ and 2½ mm. Each set of three was of equal thickness within 1 μ .

During the actual measurements the upper [plate] and the guard plate are kept at the same temperature. For the control of this condition four constantan wires are attached to the positions 1 to 4 [not shown], while a fine copper wire connects the upper plate and guard plate at 5 and 6 [not shown]. This provides for the use of six thermocouples.

After assembling the whole unit, it is hung with three telescoping studs from the lid of the high pressure reservoir. When lowered in this reservoir, the studs telescope and compress the springs, which in turn press the conductivity cell against the bottom of the steel vessel.

In the center of the lid an area of about 5 cm in diameter is ground optically flat. In this area twelve holes are drilled in the lid. They allow the twelve electrical leads to pass through it with a pressure-tight insulation.

The upper plate is heated at a higher temperature than the lower, the temperature difference established is determined from the electrical resistances of the embedded wires.

These resistances are connected as two arms of a Wheatstone bridge, and the temperature difference between the upper and lower plate is measured directly. The temperature difference between the upper plate and the guard plate is negligibly small. The constantan wires at positions 1 and 2 and at 3 and 4 were connected so as to form parallel thermocouples. The thermal voltage from these controlled the current to the guard plate through a galvanometer and photoelectric relay. With this design, the heat flow across the test gas was equal to the heat developed in the upper plate with no appreciable heat losses. This heat flow was corrected for radiant-heat transfer to give the value of q_c . The effective area *A* was calculated. In order to allow for the radiation correction, the temperature difference across the gas layer, and the effective area, three series of measurements were made with three distances between the upper and lower plates. The thermal conductivity was calculated from the measurements of distance between the plates, diameter and thickness of the upper plate, inner diameter of the guard ring, and resistance and potential-difference measurements.

A concentric-cylinder method suitable for direct measurement has been devised by Keyes and Sandell.⁴⁴ The annular gas layer is vertical and 0.025 in. thick. Special provisions are made for measurements on steam. The cell was used at temperatures to 350°C. The design avoids several of the limitations of the hot-wire method. The gas layer is not

⁴⁴ F. G. Keyes and D. J. Sandell, *Trans. ASME*, 72:767 (1950).

thin enough to avoid either convection currents near the critical point or the separation of the components of a gas mixture due to thermal diffusion.

Indirect Method. The hot-wire method is satisfactory at low pressures, and accurate measurements of the thermal conductivity of gases are available from this method. A concentric-cylinder method has been developed by Lenoir, Comings, and Junk^{45,46} for high pressures. The

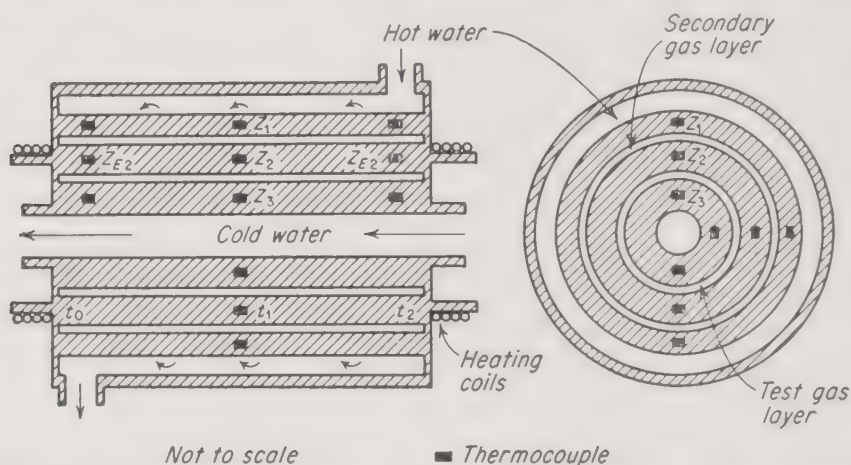


FIG. 7-20. Concentric-cylinder type of thermal-conductivity cell. [From J. M. Lenoir and E. W. Comings, *Chem. Eng. Progr.*, **47**:223 (1951).]

cell used is horizontal. It is calibrated by using several gases at atmospheric pressure. The thermal conductivity of these gases is known from measurements by others. The method provides a means for determining the thermal conductivity at high pressures by comparing a gas under high pressure with one at atmospheric pressure. The annular gas layer is thin and avoids natural convection under conditions approaching the critical. There is no indication that mixtures are separated by thermal diffusion. The only measurements needed to determine the thermal conductivity are measurements of temperature. The apparatus is described by the investigators as:

The apparatus was constructed of concentric steel tubes (SAE 1015) 30 in. in length. [Figure 7-20] shows the basic principle of the design. The apparatus was made of four horizontal steel tubes each concentric with the other, and with annular gaps between them. Cold water was pumped through the innermost tube; hot water, through the outermost annulus. Between the innermost tube and the next larger tube was the sample gas layer, 0.008 in. thick. Between the second and third tubes was a second annular gas layer 0.033 in. thick which was filled with nitrogen, methane, or helium at 1 atm pressure. Temperatures were measured by thermocouples designated by the letter Z. The function of the

⁴⁵ J. M. Lenoir and E. W. Comings, *Chem. Eng. Progr.*, **47**:223 (1951).

⁴⁶ W. A. Junk and E. W. Comings, *Chem. Eng. Progr.*, **49**:263 (1953).

second gas layer was to increase the thermal resistance between Z_1 and Z_2 to a magnitude equal to the thermal resistance between Z_2 and Z_3 .

Heat flowed from the hot water, across the series of concentric steel tubes and gas layers, to the cold water. The central tube (thermocouple location Z_2) received heat by conduction through the gas layers surrounding it, and also by conduction through the metal seals at the ends of apparatus. These metal seals had a thermal conductivity of the order of 2000 times that of the gases, and tended to act as short circuits for the heat flow. By making the low pressure seal relatively small in area and the high pressure seal larger in area, an approximate balance of thermal resistances was obtained so that the end temperatures, t_0 and t_2 were approximately the same as the middle temperature, t_1 . Metal fins were placed at both ends of this central tube with heating or cooling coils. By controlling the heat introduced in these coils, t_0 and t_2 were brought to the same temperature as t_1 , to within 0.1°F without difficulty. The middle temperature, t_1 , was not sensitive to the end temperatures. With such thin gas layers and all metal construction the radial heat flow was large, of the order of 100 Btu/hr, which minimized the effect of end-temperature differences on the readings of the central thermocouple, Z_2 .

It was desirable that the thickness of both gas layers be as uniform as possible. The surfaces were precision-honed to a mirror finish. The tubes were mounted inside one another by using shims at the ends. Uniformity of the gas layer thickness was checked by directing a light into the gas layer space at one end and noting the illuminated circle at the other end. Nonuniformity of the gas space anywhere along the length resulted in darkening of the circle along that side. This was corrected by springing the tube slightly.

An assembly drawing of the high pressure inlet end of the apparatus is shown in [Fig. 7-21]. Seven tubes were actually used. One served as a hot-water jacket. The other six were made into three tubes by press-fitting the larger over the smaller. This was done to permit construction of the thermocouple wells, which were $\frac{1}{8}$ - by $\frac{1}{8}$ -in. slots. Nine were 15 in. long, and six were 6 in. long. The long ones were used to measure temperature in the middle of the apparatus where end effects have a minimum influence on temperature. The short ones were used to measure end temperatures. The press fit construction is denoted by a change in crosshatching and the thermocouple well locations are shown by the dotted lines. Three sets of thermocouples were used to measure the middle temperatures corresponding to the top, side, and bottom positions in the apparatus.

The principles supporting the design are explained as:

Under certain conditions and after a steady state has been reached the reciprocal of the thermal conductivity of the sample gas bears a linear relationship to the ratio of the temperature differences across the inner and outer thermal resistances. These are the resistances that lie between thermocouples Z_2 and Z_3 and between Z_1 and Z_2 respectively. These conditions are listed below and will be discussed in turn.

1. In the region midway between the ends of the apparatus the radial heat

flow through the outer resistance of the apparatus is equal to the heat flow through the inner resistance.

2. The thermal conductivity of the test gas alone changes with pressure, and the thickness of this layer remains constant.

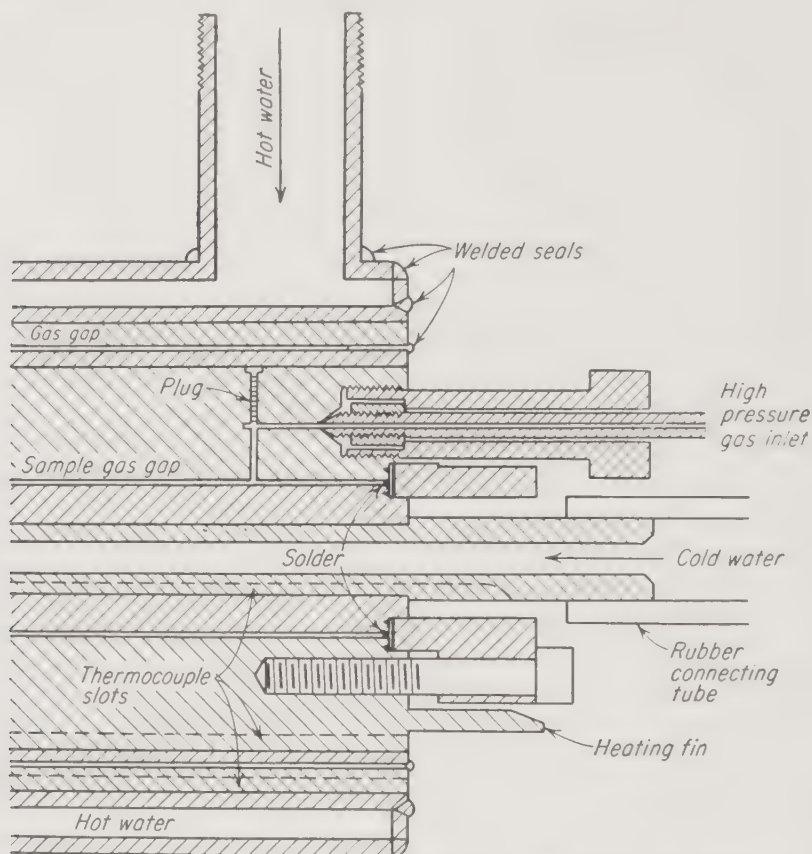


FIG. 7-21. Inlet end of thermal-conductivity bomb. [From J. M. Lenoir and E. W. Comings, *Chem. Eng. Progr.*, **47**:223 (1951).]

3. The apparatus is sufficiently symmetrical so that the heat flows through the respective resistances in series and the effect of circumferential heat flow is negligible. In particular, the effective width of the sample gas layer is independent of the thermal conductivity of the gas.

4. The radiation error is negligible.

5. Convection in the gas layers is absent.

Each of these conditions is met by the design. Condition 1 is nearly met by employing the secondary heating and cooling coils on the ends, so that the temperature gradient along the length of the apparatus is very small. The cell was designed with sufficient length to provide significant resistance in this direction. A slight correction was applied to account for any remaining small temperature gradient along the length. Condition 2 is met by adjusting the measurements for a small increase

in the high pressure-gas layer thickness due to elastic expansion of the steel cylinder with increase in pressure. Condition 3 was shown to be unimportant since the method is insensitive to rather large deviations from symmetry in spacing one tube within another. The radiation error is completely taken into account by the calibration. Tests demonstrated that natural convection was not encountered under the condition used for the measurements. The conditions which lead to convection in gases under high pressure will be considered in Chap. 9.

The cell was calibrated for use with a single gas in the outer annulus. About four different gases whose thermal conductivity is known were employed in the inner annulus. If the temperature difference between thermocouples Z_2 and Z_3 is designated by Δt_x and that between Z_1 and Z_2 by Δt_N , then it can be shown⁴⁶ that there is a unique relationship between the ratio of these temperature differences and the reciprocal of the thermal conductivity of the gas in the inner annulus expressed by

$$\frac{\Delta t_x}{\Delta t_N} = f\left(\frac{1}{k}\right)$$

This relationship is established from the measurements of Δt_x and Δt_N and the thermal conductivities of the four calibration gases. When a gas with an unknown thermal conductivity is placed in the inner annulus, measurement of Δt_x and Δt_N is sufficient to determine its thermal conductivity.

7-6. Reactors. Many of the mechanical design features of chemical reactors and the control of reaction rates are discussed in other chapters. Techniques of operation and the general classes of reactor systems are described here. Chemical reactions are carried out under high pressures in autoclaves operated batchwise or with continuous flow, in pipeline continuous-flow-type reactors, or in continuous-flow reactors containing a stationary catalyst bed. The design of the mixer frequently has an important effect on the rate of a chemical reaction in an autoclave.^{46a}

Autoclaves. Mixing of the contents of an autoclave is a greater problem at high pressures than at low. Propellor- or turbine-type impellers driven by a shaft which passes through a packing gland are available in standard designs for pressures up to about 5,000 psi. When the lubrication of the packing gland may introduce undesirable impurities, the packing gland may be avoided and mixing may be obtained by electromagnetic means such as the Magne Dash.⁴⁷ At higher pressures a rocker or shaker mechanism may be used. Two autoclaves equipped for mixing

^{46a} J. H. Rushton and J. Y. Oldshue, *Chem. Eng. Progr.*, **49**:161, 267 (1953); J. H. Rushton, *Chem. Eng. Progr.*, **50**:587 (1954).

⁴⁷ Catalog 200, Autoclave Engineers Inc., 1952.

are illustrated in Figs. 7-22 and 7-23. Hoffmann, Montgomery, and Moore⁴⁸ investigated the mixing in experimental rocker-type and shaking autoclaves in glass apparatus at atmospheric pressure. The rate of

hydrogenation of nitrobenzene was used as a criterion of the effectiveness of mixing. The two types of mixers are shown schematically in Figs. 7-24 and 7-25. The rocker type is not very satisfactory for some reactors.

The major factors influencing agitation in the rocker type were the speed of rocking and the angle of rocking.

At extremely slow rates of oscillation, there was little or no turbulence, either within the liquid or between the liquid and the gas. The liquid flowed evenly down the incline caused by the rocking, cushioned itself against the

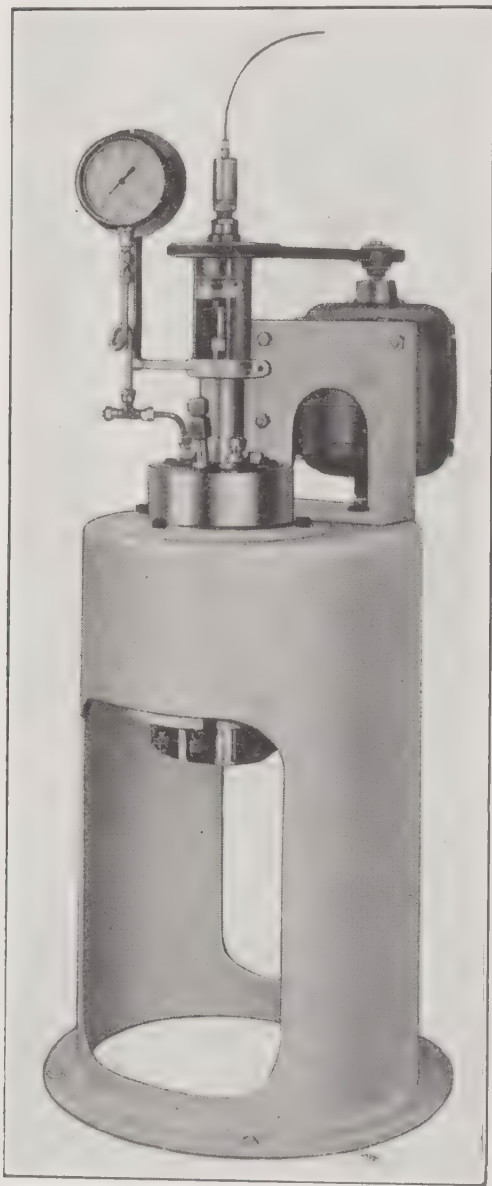


FIG. 7-22. Autoclave with propellor-type agitator. (Autoclave Engineers Inc.)

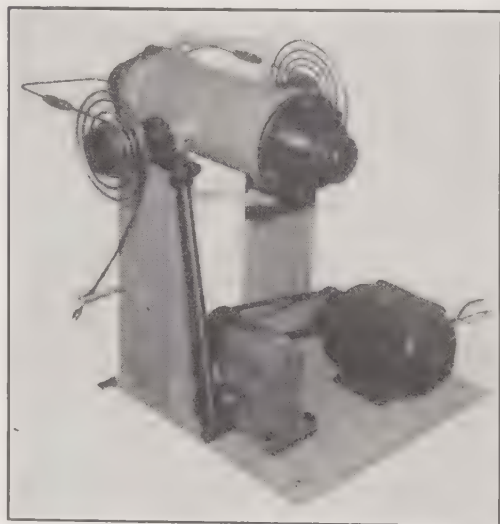


FIG. 7-23. Autoclave with rocking mechanism. (Autoclave Engineers Inc.)

end of the tube, and reversed its even flow as the reactor motion changed direction. The powdered charcoal which was added as a visual aid settled out on the bottom of the tube.

⁴⁸ A. N. Hoffmann, J. B. Montgomery, and J. K. Moore, *Ind. Eng. Chem.*, **40**:1708 (1948) and **41**:1683 (1949).

As the rate of rocking was increased slightly, turbulence began to occur within the liquid, as evidenced by the uniform dispersion of the charcoal. However, there was still very little gas-liquid mixing. At a somewhat higher rate of rocking a very pronounced gas-liquid turbulence or mixing began to appear. This very effective mixing was caused by the sudden stopping of the liquid flow

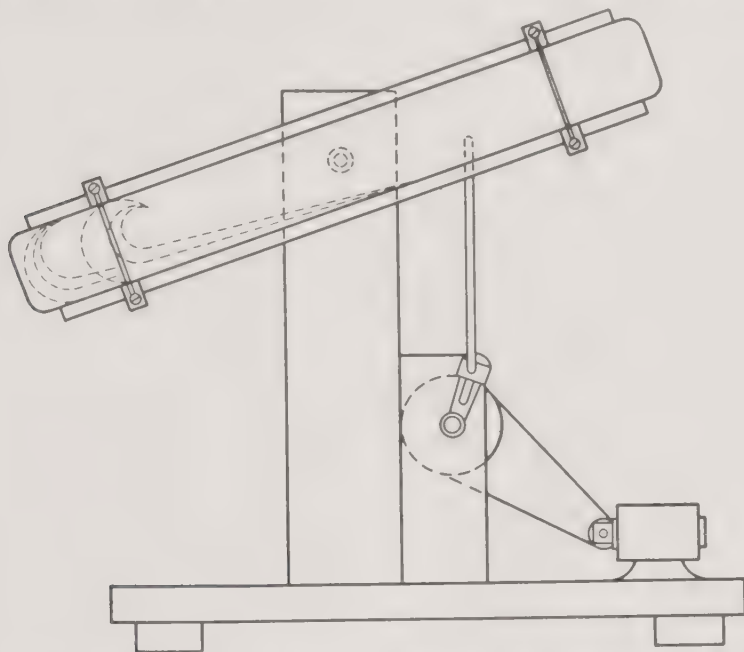


FIG. 7-24. Action with rocker-type agitator. [From A. N. Hoffmann, J. B. Montgomery, and J. K. Moore, *Ind. Eng. Chem.*, **40**:1708 (1948); and **41**:1683 (1949).]

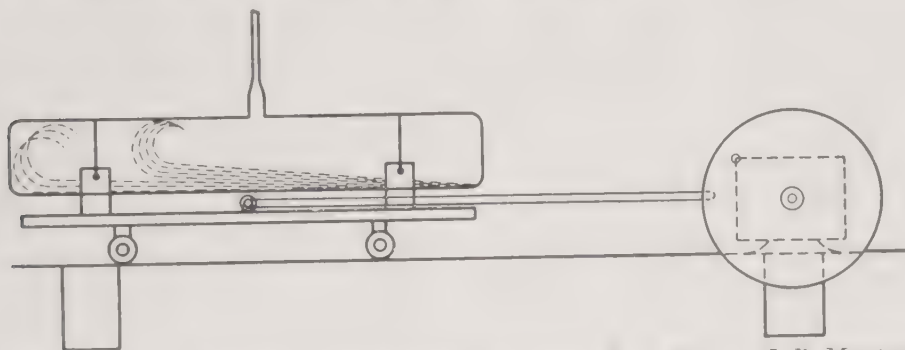


FIG. 7-25. Action with shaker-type agitator. [From A. N. Hoffmann, J. B. Montgomery, and J. K. Moore, *Ind. Eng. Chem.*, **40**:1708 (1948); and **41**:1683 (1949).]

at the termination of each half oscillation, and can best be described as a breaking over of the wave crest of the liquid in the end of the reactor, during which gas was enveloped and mixed with the body of the liquid.

As the rate of rocking was further increased, this pronounced gas-liquid turbulence (or gas enveloping effect) reached a maximum and gradually decreased until, at very fast rocking rates, the breaking over of the wave crest disappeared and the liquid surface remained unbroken except for a few ripples. At these

fast rates of rocking beyond which the gas envelopment had ceased, the inertia of the liquid prevented its flow from one end of the reactor to the other, and the liquid surface remained essentially parallel to the long axis of the reactor tube. As the turbulence decreased, the suspended charcoal first concentrated in the center of the reactor, and later, at the fastest rates of rocking, settled out on the bottom of the reactor. For a 30° angle of rocking, the maximum hydrogenation rate at 35 oscillations per minute was approximately four times the rate at either 15 or 60 oscillations per minute.⁴⁸

The shaking-type autoclave gave better mixing. The maximum hydrogenation rate was approximately three and a half times as fast

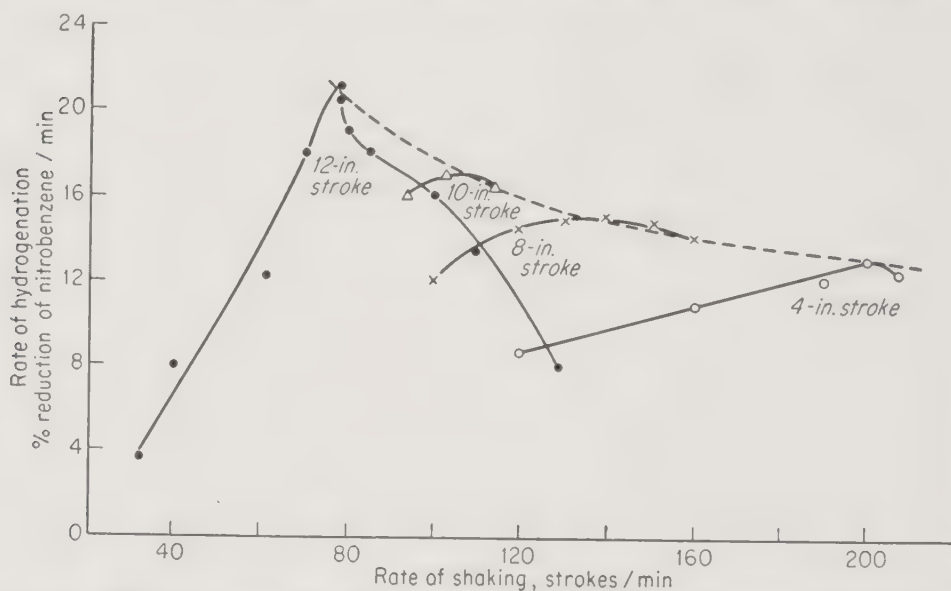


FIG. 7-26. Effect of shaking on hydrogenation rate with several stroke lengths. [From A. N. Hoffmann, J. B. Montgomery, and J. K. Moore, *Ind. Eng. Chem.*, **40**:1708 (1948); and **41**:1683 (1949).]

as the best rate with the rocking-type mixer. The major factors influencing mixing in the shaking type are rate of shaking, stroke length, and reactor volume in any given length-diameter ratio. The behavior of the contents of the reactor as the rate of shaking was increased was analogous to that found in the rocker type when using the shorter stroke lengths, from 3 to 6 in. With longer stroke lengths, of 8 to 12 in., turbulence did not decrease at the higher shaking rates. The liquid was broken into fine drops, and very little remained in the liquid layer as it was hurled from one end of the reactor to the other with the sudden reversal of the reactor's motion. Nevertheless, the hydrogenation rate passed through a maximum and decreased again at the higher agitation rates. This behavior is shown in Fig. 7-26. Apparently the gas-enveloping action is the key to improved hydrogenation rates. Turbulence, although apparently more violent, does not furnish the best gas-liquid mixing con-

ditions for optimum hydrogenation rates when the conditions for gas envelopment are not present. Figure 7-26 shows clearly the extreme effects of various mixing motions on a chemical reaction. Rotating turbines and Magne Dash motions would be expected to compare favorably with the shaking type.

Pipeline-type Reactors. A tube with small inside diameter and moderate wall thickness will withstand high pressures. It provides a convenient form of vessel for carrying out a chemical reaction when the reactants are in a single phase or in a homogeneous slurry. The control of temperature is easy because of the extensive surface for heat transfer. The reactants flow through the coil essentially without longitudinal mixing, and the rate of reaction is reduced by the products of the reaction as these are formed in the travel along the tube. Reactions should be avoided which deposit coke or other solid matter and block the tube. A tubular reactor⁴⁹ is shown in Fig. 7-27. The reactor was fabricated from $\frac{9}{16}$ -in. chromium-molybdenum alloy steel tubing (SAE 4130) and was designed for operation at 15,000 psi and 950°F. It was helical in shape and contained 14.5 loops of 8 in. diameter and 2 in. pitch. The inlet lead came through the center of the helix and supported an Alundum tube on which the heating elements were wound. The coil was inserted in a furnace made of Armstrong A-16 insulating brick. Three iron-constantan thermocouples were silver-soldered to the coil. The couples and short adjacent lengths of the coil were wrapped with aluminum foil to reduce radiation errors. The couples were connected to controlling potentiometers. The heated volume of the reactor was 170.5 cu cm.

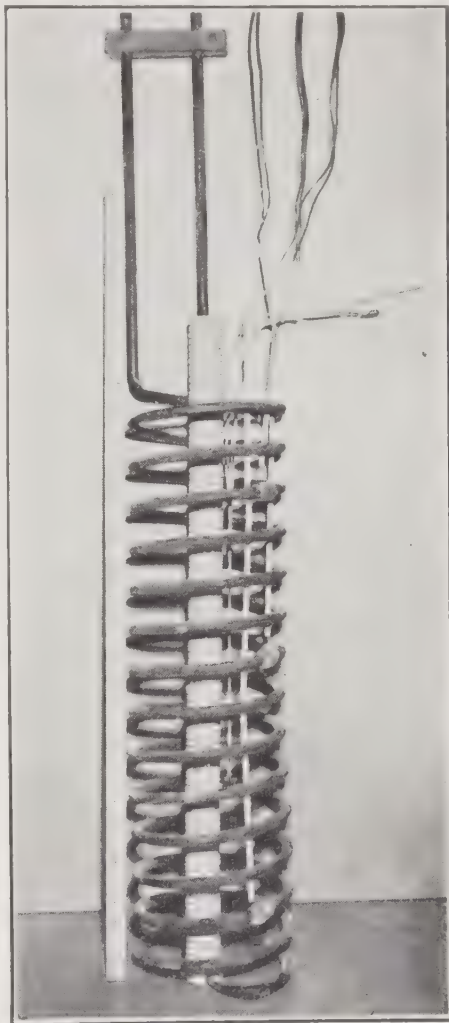


FIG. 7-27. Coil reactor. [From J. E. Knap, E. W. Comings, and H. G. Drickamer, *Ind. Eng. Chem.*, **46**:708 (1954).]

⁴⁹ J. E. Knap, E. W. Comings, and H. G. Drickamer, *Ind. Eng. Chem.*, **46**:708 (1954).

The feed mixture was contained in forged-steel storage cylinders and fed to the reactor at a controlled rate by pumping water into the bottom of one cylinder at a time. An Aminco 30,000-psi plunger pump placed SAE 10 motor oil under pressure, and this displaced water from another cylinder. The water in turn displaced the feed mixture. The rate of feed was measured by observing the time and volume of oil pumped from a graduated cylinder. The pressure in the system was controlled by an Autoclave Engineer's 30,000-psi metering valve at the discharge end of the coil. The product from the reactor was throttled to atmospheric pressure and passed through a suitable collection system.

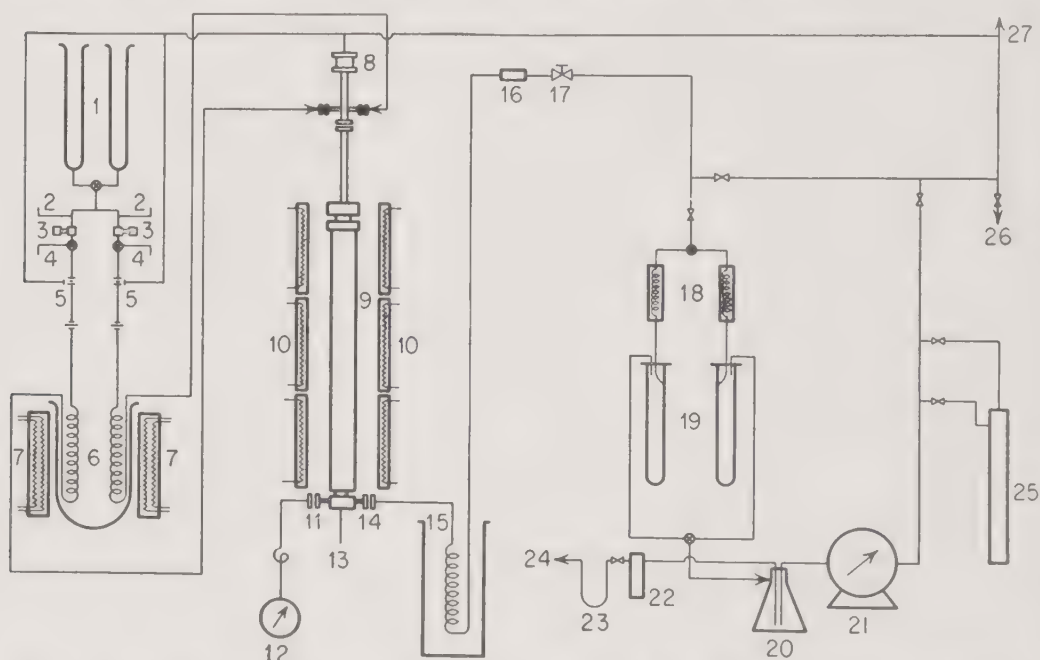


FIG. 7-28. Catalytic reactor in flow system. [From C. M. Sliepcevich and G. G. Brown, *Chem. Eng. Progr.*, **46**:556 (1950).]

Catalyst-bed Reactors. An experimental reactor employing a bed of catalyst and operated continuously at 10,000 psi and 1200°F was built by Sliepcevich and Brown.⁵⁰ It was estimated that the design was suitable for operation at 20,000 psi at a lower temperature, around 1000°F. The catalytic decomposition of butanol-1 was carried out in the equipment. The design as described by the investigators is as follows:

A schematic flow diagram of the equipment is shown in [Fig. 7-28]. Two 500-ml graduated cylinders (1), connected by a three-way stopcock act as feed reservoirs for the dual feed, plunger-type, Hills-McCanna pump (3). The pump is equipped with suction risers (2), and discharge risers (4), which serve to prevent vapor-lock or air binding in the pump cylinder. Two Aminco rupture disc

⁵⁰ C. M. Sliepcevich and G. G. Brown, *Chem. Eng. Progr.*, **46**:556 (1950).

assemblies (5), are located immediately downstream from the pump and are vented to the central venting system which exhausts to the outdoors (27).

Two 30-ft coils of stabilized stainless steel tubing, Type 321, $\frac{1}{4}$ -in. OD by 0.085-in. ID, are located in an Eclipse pressed steel pot which serves as a preheater and is filled with DuPont heat treating salt No. 1. The pot is heated by means of chromel resistance wire embedded in an alundum core (7).

The two feeds from the heater, then fed to the reactor, are purposely not allowed to mix until they reach the reactor in order to minimize thermal, non-catalytic reactions in the preheater.

The reactor (9) is machined from a forging of Uniloy 19-9 WMo (highly alloyed stainless steel) and is about 3 ft long. The inner diameter of the reactor is $\frac{3}{4}$ in. and its outer diameter is $2\frac{1}{2}$ in. The reactor is equipped with a Black, Sivalls, and Bryson special safety head of stainless steel (8) and is also vented to the central vent line (27). Three separate radiant furnaces serve as reactor heaters (10). Each heater consists of chromel wire embedded in an alundum cement core. The heat input to each heater unit is controlled separately by means of three Adjustavolts.

The bottom of the reactor is fitted with a $\frac{1}{4}$ -in.-OD \times $\frac{3}{32}$ -in.-ID stainless steel thermocouple tube (13), which extends the whole length of the reactor. A traveling thermocouple wire embedded in a two-holed ceramic insulator, permits measurement of the temperature over the full length of the reactor.

The salt pot and reactor furnaces are enclosed in a single housing. Firebrick and silocel are used as insulation. Each heater unit and the salt bath are equipped with chromel-alumel thermocouples.

The outlet from the bottom of the reactor includes a pressure gage connection (12) and a connection to the condenser (15). The condenser consists of coiled stabilized stainless steel tubing, $\frac{1}{4}$ in. OD \times 0.085 in. ID and a water box cooler. The condenser line extends to a filter (16) and a stainless steel Aminco needle valve (17) by means of which the pressure on the entire apparatus is controlled.

Copper tubing, $\frac{1}{4}$ in. OD, connects the valve to the sampling manifold which is provided with proper by-passes of rubber tubing, brass valves, and glass stopcocks in order to provide a completely enclosed sampling system. In normal operation the discharge from the condenser passes to two vertical glass condensers (18) and then to two liquid-product, graduated, receivers (19). The gas passes overhead from these two 500-ml receivers to an entrainment separator (20). The gas then is metered in a Sargent wet-test meter (21), and exhausts through the central venting system (27).

A mixture of 50 g of bead catalyst and 80 g of zirconite chips was placed in the reactor to a depth of about 17 in. The purpose of the zirconite chips was to dilute the catalyst and thereby facilitate more uniform temperature regulation over the catalyst bed during the endothermic reaction. The average temperature variation over the entire catalyst bed at any instant did not exceed 10°F .

Another design for a catalyst-bed reactor is described by Adams and Comings.⁵¹ The synthesis of ammonia was carried out in this apparatus.

⁵¹ R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).

The reactor was designed for 15,000 psi and 950°F. A schematic diagram of the apparatus appears in Fig. 7-29. Hydrogen and nitrogen from commercial cylinders were mixed in the desired proportions in a gas holder. After the mixture was drawn from the holder, it was compressed by a three-stage gas compressor and hydraulic booster compressor. This compressed gas was stored in two forged-steel cylinders at pressures of several hundred pounds per square inch higher than the pressure in the

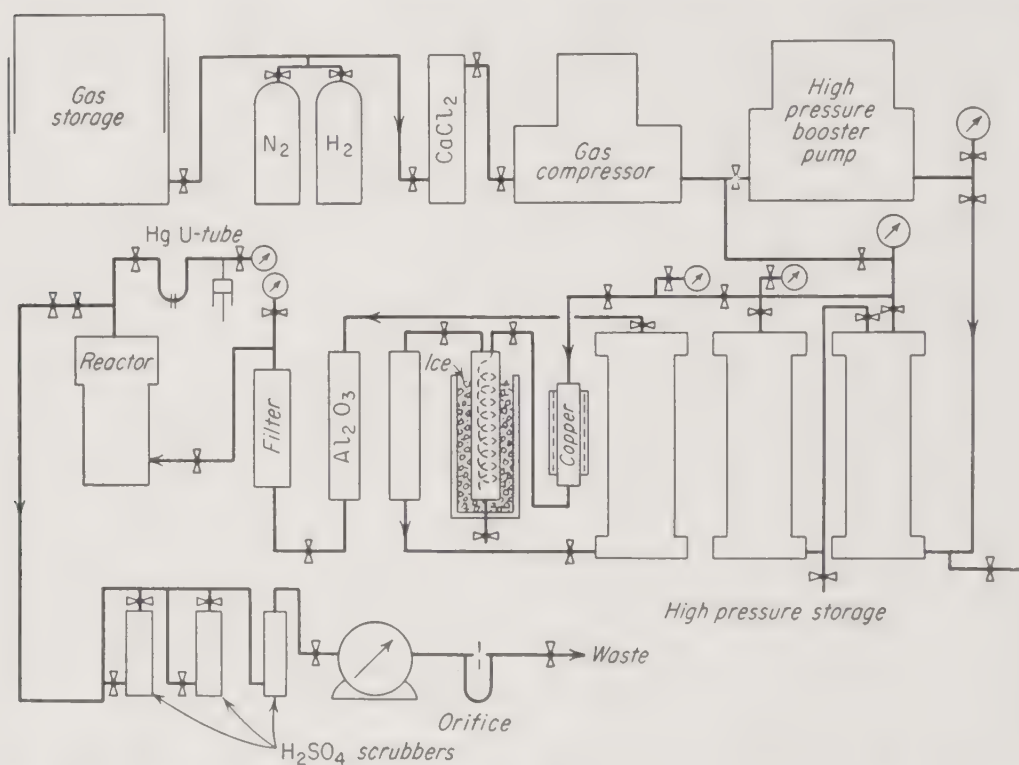


FIG. 7-29. Catalytic reactor in flow system. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

remaining part of the system. A needle valve between the storage cylinders and the reaction system was used to maintain a constant pressure in the reactor for a given rate of flow through the catalyst bed. From storage, the gas entered the purifying train where oxygen, water vapor, carbon dioxide, dust, and oil were removed. The pure gas passed into the reactor and through the catalyst. The gaseous products were reduced to atmospheric pressure in one stage by a needle valve, and the ammonia was scrubbed out. The ammonia-free gas escaped to the atmosphere.

The reactor was constructed of SAE 6150 chrome-vanadium steel and was designed to withstand an internal pressure of 15,000 psi at 500°C. The steel had a yield point of 106,000 psi at 700°F. The design was based on the maximum-strain theory of elastic failure. The inside diam-

eter of the reactor was 1.625 in., the outside diameter was 5 in., and the over-all length was 17 in.

Figure 7-30 is a simplified diagram of the reactor and its internal parts. The cold-gas feed entered through the bomb wall at a point near the bottom of the reactor and by means of a copper inner tube was sent up along the inside walls of the vessel. The gas then passed down over an electric heating coil, up again through the catalyst bed, and out of the reactor. The heater was wound more closely near the head of the bomb than lower on the catalyst-support tube in order to decrease the

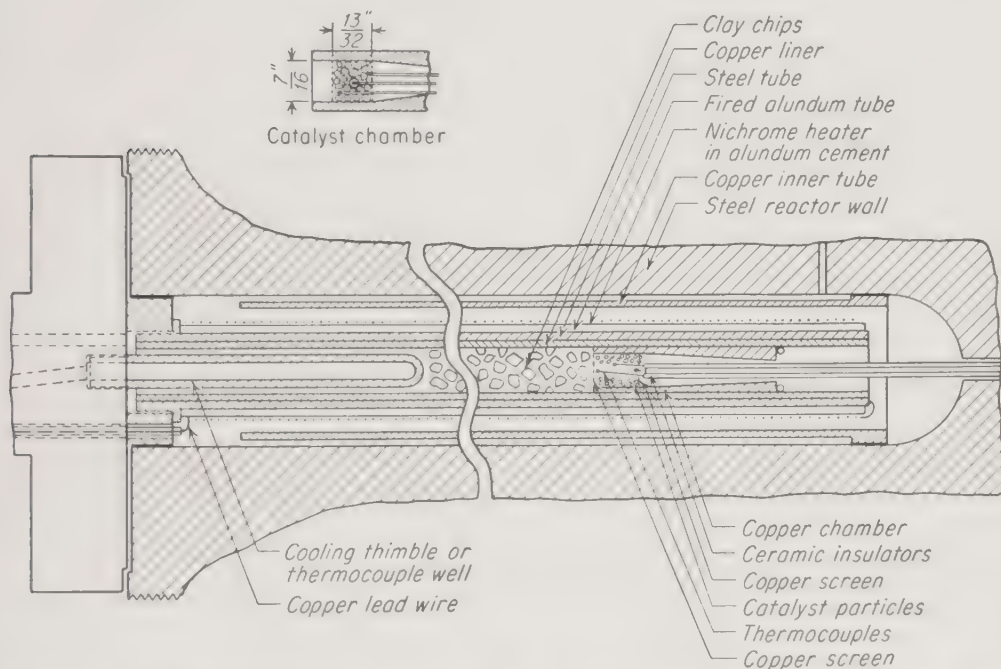


FIG. 7-30. Interior of reactor. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

temperature gradient caused by the flow of heat along the tube to the bomb head.

The catalyst chamber was made of copper and had a volume of 0.061 cu in., or 1 ml (0.38 in. diameter by 0.5 in. long), when the thermocouple assembly was in place. Three iron-constantan thermocouples were inserted in the catalyst bed, one at the bottom of the bed, another just above the top of the bed, and a third in a catalyst pellet at the center of the bed. The thermocouple leads were brought out through the bottom of the bomb and passed through a length of high-pressure tubing to a steel block. The electric-lead seals were fitted in this block where the temperature was low. Heat transfer in the area of the catalyst bed was good enough to keep the readings of the three thermocouples constant within a range of 1 to 3°; the two lower couples were usually within 1° of

each other. The temperature of the catalyst bed was controlled by regulation of the power input to the heater, so that the heat loss from the bomb kept the bed at the required temperature.

Purification of the gases was accomplished by passing them successively through a hot-copper-gauze deoxidizer, ice condenser, soda-lime tower, magnesium perchlorate tower, ballast cylinder, activated-alumina tower, and sand filter.

Preparation and Control of Feed to Reactors. The reactants charged to high-pressure reactors are of several classes:

1. Liquids of low volatility
2. Liquids of high volatility
3. Gases and mixtures of gases
4. Combinations of gases and liquids
5. Combinations of liquids and solids

Liquids of low volatility may usually be fed with a plunger-type pump. Modifications of small pumps of this type are described by Henriques.⁵²

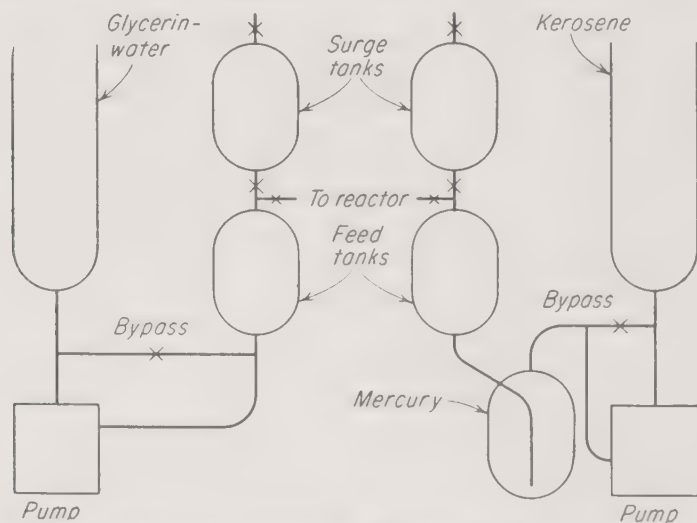


FIG. 7-31. Two displacement arrangements. [From H. J. Henriques, *Ind. Eng. Chem.*, **39**:1564 (1947).]

This type of feed system is used in Sliepcevich's reactor which has already been described.

Highly volatile liquids or liquefied gases are handled more satisfactorily by displacing them from a closed vessel with an immiscible liquid. The pump acts on this liquid. This method avoids leaks of the feed liquid, which would be difficult to detect. Two displacement arrangements suggested by Henriques⁵² are shown in Fig. 7-31.

⁵² H. J. Henriques, *Ind. Eng. Chem.*, **39**:1564 (1947).

The simpler, at the left, employs a glycerol-water solution as the displacement liquid. Before starting operations, the lines and feed tank must be filled to a point near the reactor. During such periods a surge tank provides expansion space. Immediately before the pump is started, the surge tank is isolated by closing the bottom valve. When glycerol-water solution is not suitable, the scheme shown on the right may be used. Mercury is not pumped directly because steel ball valves float in it. On the other hand, kerosene behaves ideally in most pumps.

A displacement arrangement was used for Knap's⁴⁹ coil reactor. In this case, the preparation of the volatile feed mixture posed special problems. The feed was a mixture of isobutane and propylene with trichloropropane as an initiator.

The three ingredients were charged to a forged steel storage cylinder. This was fitted with a removable plywood box insulated with hair felt. The box was filled with crushed dry ice. The hydrocarbons were received in 28-gal cylinders. The isobutane cylinder was placed on a platform scales and was surrounded by a steam coil in a galvanized iron shield. The coil and shield did not rest on the scales. Isobutane was weighed directly in the heated cylinder and delivered to the cooled cylinder. A more accurate method of weighing was used for the smaller charge of propylene. This was first transferred to a small evacuated bomb submerged in a large stainless-steel Dewar flask containing liquid nitrogen. This bomb and Dewar flask were weighed together and the weight of the propylene was determined by difference. The propylene was then transferred to the storage cylinder by removing the liquid nitrogen and allowing it to warm up. The initiator was placed in a small bomb and flushed into the cylinder by passing part of the propylene through this bomb. The contents of the storage cylinder were allowed to warm up to room temperature. Then a uniform feed mixture was assured by pumping water into the bottom of this cylinder and displacing the contents to another cylinder. This procedure was then reversed and the mixture displaced from the second cylinder to the first cylinder.

Gas flow rates are regulated by a needle valve as in Adam's apparatus or by passing them through a capillary-tube flowmeter.⁵³ When low rates of flow are desired, of the order of a few cubic centimeters per minute, displacement by a liquid provides a more precise control although the gas temperature and pressure must then be held constant.

Reactions between gases and liquids require a dual feed system, one for each phase, when the unit is operated continuously. The gas may be introduced at the bottom of a cylinder and bubble up through the liquid, or the two may be shaken in an autoclave.

When the liquid feed contains a solid in suspension, provision is required to avoid clogging the feed pump or the transfer lines. A dis-

⁵³ E. L. Clark, P. L. Golden, A. M. Whitehouse, and H. H. Storch, *Ind. Eng. Chem.*, **39**:1555 (1947).

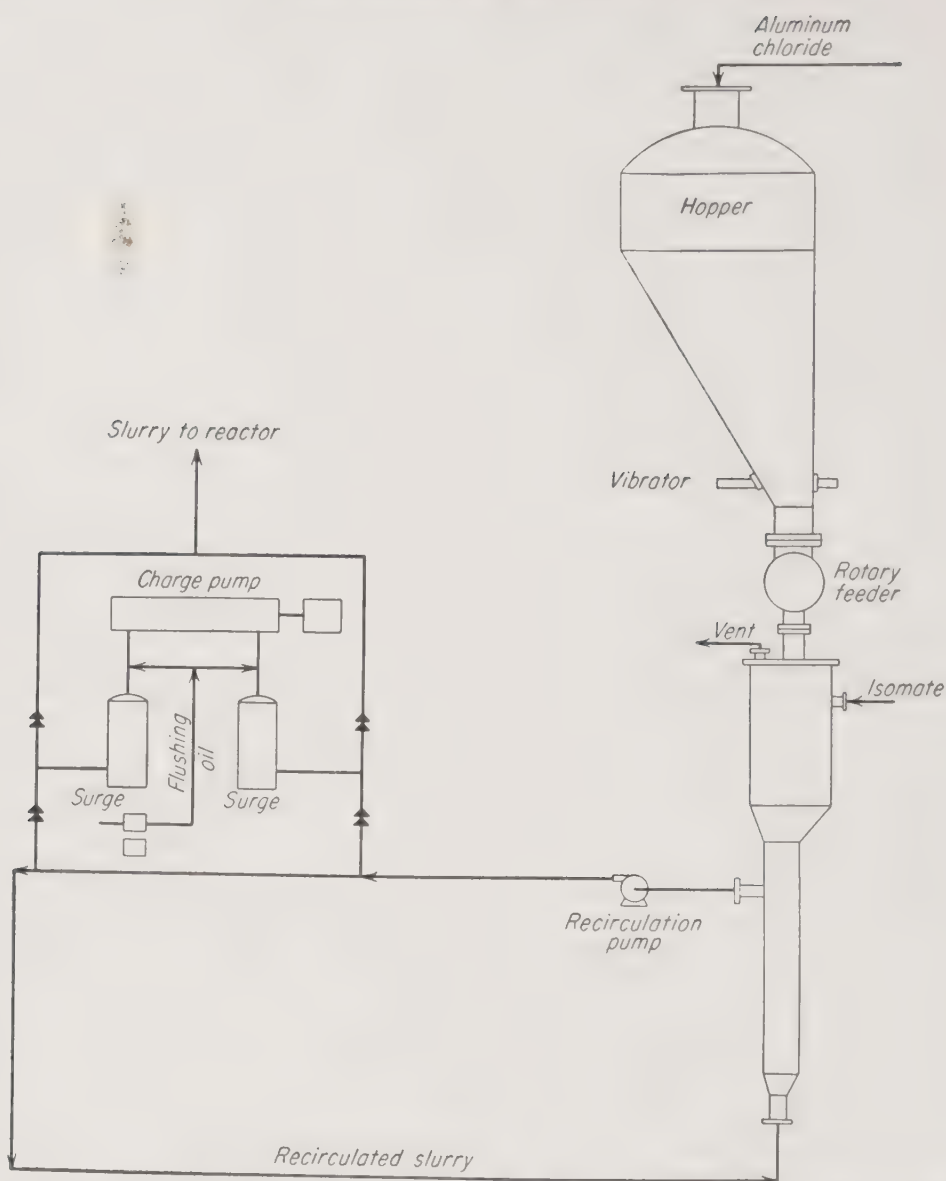


FIG. 7-32. Slurry-feeding system. [From J. W. Swearingen, R. D. Geckler, and C. W. Nysewander, *Trans. Am. Inst. Chem. Engrs.*, **42**:573 (1946).]

placement system was devised by Swearingen, Geckler, and Nysewander⁵⁴ for the Isomate process. This system is shown in Fig. 7-32, and its operation is as follows:

Transfer of solid AlCl_3 from atmospheric pressure to the reactor pressure of 700 to 850 psi was a perplexing problem in designing the first commercial installation, but the injection of AlCl_3 -naphtha slurry as finally adopted has proven quite satisfactory. Granular AlCl_3 of 18 to 100 mesh falls from the storage

⁵⁴ J. W. Swearingen, R. D. Geckler, and C. W. Nysewander, *Trans. Am. Inst. Chem. Engrs.*, **42**:573 (1946).

hopper through a rotating star feeder to the slurry tank. Here it is mixed with incoming Isomate by means of a centrifugal pump circulating the tank contents from bottom to top through the slurry loop line. Slurry is injected into the reactor by a double-acting plunger-type pump which takes suction on the slurry loop line. Aluminum chloride is prevented from entering the slurry pump cylinder by using check valves in the lines and surge chambers between the valves and the pump cylinder. The surge chambers are continually flushed with a small quantity of Isomate. The slurry pumping scheme is conventional for handling hot oil, and no difficulty has been experienced in this adaptation as long as the slurry and flush oils are kept dry and free from olefins. Linear velocities of 1 ft/sec in vertical lines and 6 ft/sec in horizontal lines are sufficient to maintain a slurry containing from 1 to 5 lb of AlCl_3 per gallon.

Extreme Conditions of Temperature and Pressure. A method for making measurements at high temperatures up to 1000°C under a pressure of 1,000 atm was described by Saurel and Vodar.^{10a} The vessel walls are maintained at a relatively low temperature by insulation inside the pressure vessel, and heat is supplied by an electric resistance inside the insulation. Pressures of 150,000 psi at 600°C have been obtained by Birch.^{54a} P. W. Bridgman⁵⁵ has discussed the various unsuccessful attempts to produce synthetic diamonds which preceded the successful work at the General Electric Company. The method used in this latter work has not been disclosed, but Bridgman states that means have been found to maintain pressures of more than 100,000 atm and temperatures of 2500°C for hours at a time. Transient pressures of the order of 5,000,000 psi have been attained using shaped high-explosive charges.^{56,57} Techniques for use at very high pressures are also described by others.^{58,59}

^{54a} F. Birch and R. R. Law, *Bull. Geol. Soc. Am.*, **46**:1219 (1935).

⁵⁵ P. W. Bridgman, *Sci. American*, p. 42, November, 1955.

⁵⁶ S. Minshall, *J. Appl. Phys.*, **26**:463 (1955).

⁵⁷ J. M. Walsh and R. H. Christian, *Phys. Rev.*, **97**:1544 (1955).

⁵⁸ A. W. Lawson, *Rev. Sci. Instr.*, **25**:1136 (1954).

⁵⁹ P. W. Bridgman, *Phys. Rev.*, **57**:237 and 342 (1940); *Proc. Am. Acad. Arts and Sci.*, **81**:165 (1952).

CHAPTER 8

GASES AND LIQUIDS

The experimental measurement of the pressure, temperature, and volume of a known weight of vapor or liquid is more readily accomplished with high precision than are the measurements of a number of other quantities. For example, the direct measurement of heat, especially under high pressures, is usually less precise than the establishment of a volume and the measurement of a temperature and pressure. It is thus desirable to make pVT measurements and from these to calculate other properties. Thermodynamics provides a basis for making these calculations, and the values so calculated can often be used with greater assurance than values measured directly.

The pVT behavior will be described. This information will be useful later in calculating the effect of pressure on a number of physical and thermal properties, on chemical equilibrium, and to some extent on chemical-reaction kinetics. It is directly applicable to the industrial storage, and to the chemical and physical processing, of gases and liquids under pressure. The phase changes from gas to liquid, liquid to solid, and gas to solid produce discontinuities in the otherwise uniform variation of the volume of a pure substance with either temperature or pressure. These phase changes will be considered first.

8-1. Phase Behavior of Pure Substances. When a known weight of a substance or mixture of substances is confined under a predetermined and sufficient set of conditions, all its properties will have definite values. If the number of predetermined conditions is too small, however, the properties of the substance will not have definite values. When sufficient predetermined conditions are imposed so that all the properties of the substance have definite values, then the substance is said to be in a reproducible state since its properties will always be the same under these conditions. The number of conditions or variables which must be predetermined depends on the number of phases present and the number of pure substances or components required to prepare the mixture. The Gibbs phase rule tells how many conditions or variables must be determined in order to ensure that the system is in a reproducible state. This is expressed as

$$\mathcal{P} + \mathcal{V} = \mathcal{C} + 2$$

(8-1)

and indicates, for example, that with a system containing one component ($\mathcal{C} = 1$) and two phases ($\mathcal{P} = 2$), only one variable ($\mathcal{V} = 1$), or condition, need be specified to ensure that all properties of the system will have values that are reproducible. Thus with a system consisting of pure water with both liquid and vapor present in static equilibrium, it is sufficient to state any one variable such as pressure, temperature, specific volume of the vapor, enthalpy of the vapor, or the like. All other intensive properties of either phase then have definite values which may be determined. With a pure substance the existence of a vapor and liquid

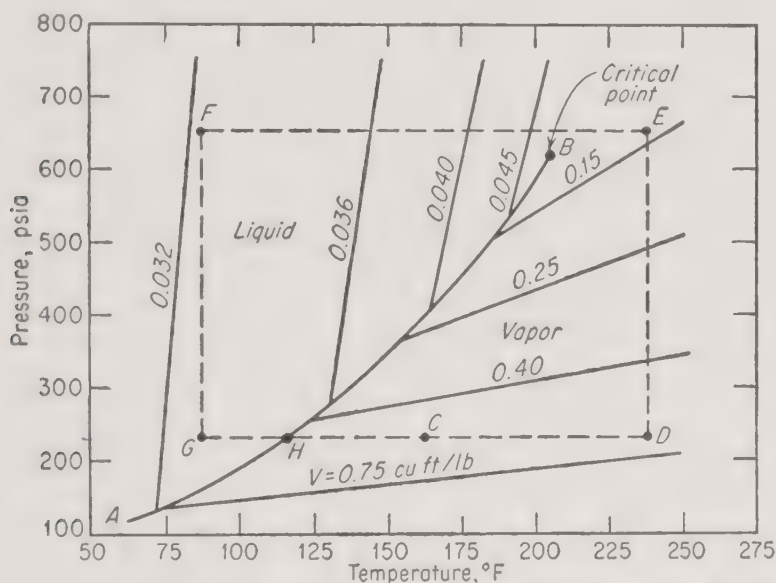


FIG. 8-1. Vapor-pressure curve and isometrics of propane. (From B. H. Sage and W. N. Lacey, "Volumetric and Phase Behavior of Hydrocarbons," The Gulf Publishing Company, Houston, Tex., 1949.)

phase in equilibrium at a given temperature renders all the properties of both phases completely definite but does not indicate the relative amounts of the two phases present. This applies at any pressure. A relationship between temperature and pressure when the vapor and liquid of pure propane are in equilibrium is shown as line *AHB* in Fig. 8-1. This line is a phase boundary line and represents the vapor-pressure, or saturation, curve which extends to the critical temperature and critical pressure indicated at *B*. Here the vapor and liquid have the same density and lose their identity as separate phases. At higher temperatures, there will be no clearly defined change from vapor to liquid regardless of how high the pressure is raised. For any combination of temperature and pressure not on a phase boundary line there will be only a single phase, and, according to the phase rule for a single component, two variables must be

specified in order that all the properties of the system will have definite values. The region below the vapor-pressure curve in Fig. 8-1 is a single-phase vapor region, and that above, a single-phase liquid region. Consider a vapor at the conditions indicated at *C*. If this is cooled so that its temperature decreases, a change to liquid will occur at *H* and the temperature will not decrease beyond that at *H* until all the vapor has condensed to liquid. This is a well-defined phase change. A similar change from liquid to vapor occurs if one heats the liquid under the conditions at *G*. The temperature at *H* is both the boiling point of the liquid and the condensing point of the vapor at the pressure along the line *GHC*.

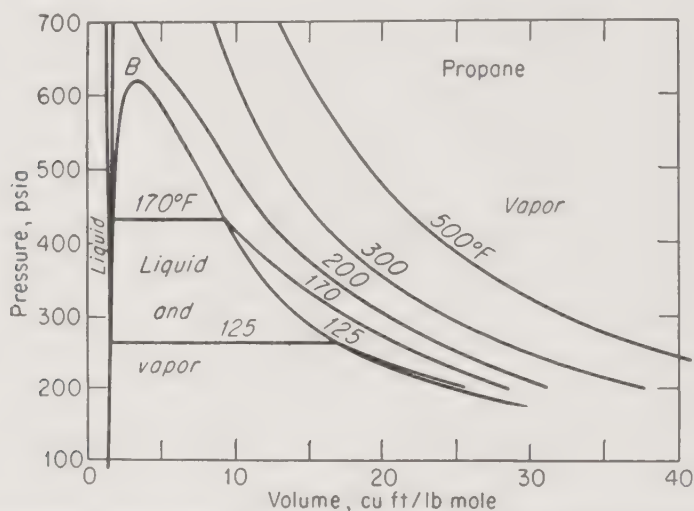


FIG. 8-2. Isotherms of propane. [From W. W. Deschner and G. G. Brown, *Ind. Eng. Chem.*, **32**:836 (1940).]

As another example, one may start with the vapor at *C* and raise its temperature at constant pressure to the temperature at *D*. Then raise its pressure at constant temperature to that at *E*. Since this temperature is higher than the critical temperature no phase change will occur. Next, lower the temperature at constant pressure to *F*, and, finally, decrease the pressure at constant temperature to the conditions at *G*. This condition was previously identified as liquid, yet no definite change in phase from the vapor to the liquid has occurred at any point in the process represented by the path *CDEFG*. A vapor has been changed into a liquid without passing through a specific temperature or pressure at which the phase change occurred.

The relationship between molal volume and pressure is shown in Fig. 8-2. The phase change from vapor to liquid results in a change in molal volume, and, except at the critical point, this difference in volume is represented by the difference between the vapor and liquid lines forming the boundary of the region in which the two phases exist together in

various proportions. A similar relationship exists¹ between the temperature and enthalpy, as shown in Fig. 8-3 where the critical point is shown at B.

Behavior of a Single Phase. With a single phase ($\Phi = 1$), two variables must be specified ($\mathcal{V} = 2$) in order to ensure that all properties of

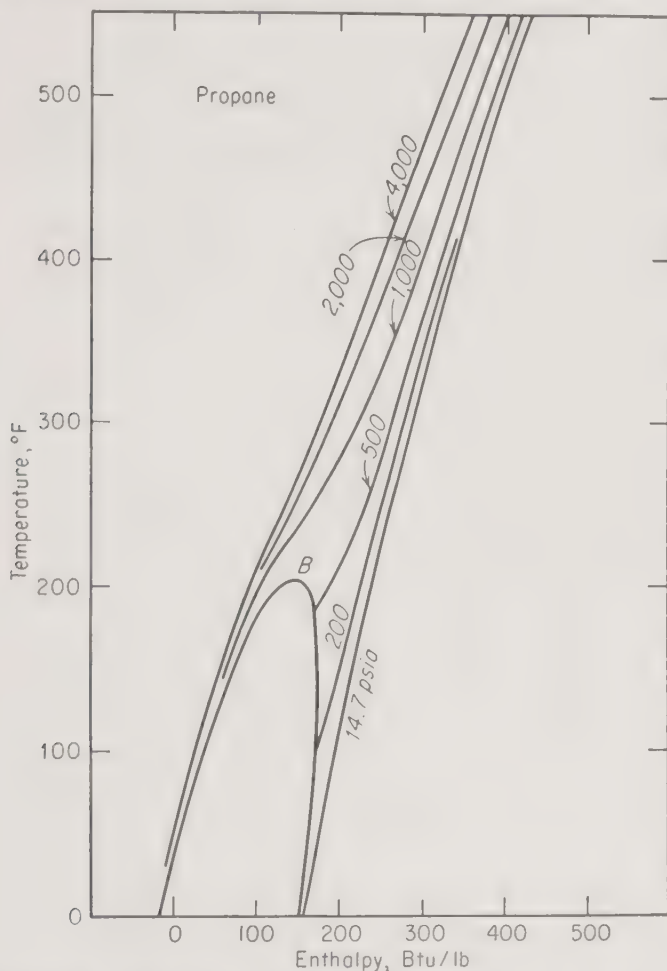


FIG. 8-3. Temperature vs. enthalpy for propane. (From C. G. Kirkbride, "Chemical Engineering Fundamentals," p. 394, McGraw-Hill Book Company, Inc., New York, 1947.)

the phase have definite values. This is the situation in Fig. 8-1 in any region not crossed by the saturation curve and in Figs. 8-2 and 8-3 outside the two-phase region. The behavior of the gas and liquid in these single-phase regions is shown by the lines of constant volume (isometrics) in Fig. 8-1, of constant temperature (isotherms) in Fig. 8-2, and of constant pressure in Fig. 8-3. Of these, the isometrics alone are nearly

¹ C. G. Kirkbride, "Chemical Engineering Fundamentals," McGraw-Hill Book Company, Inc., New York, 1947.

straight lines. This observation will be used later in fitting the behavior of real gases to a mathematical equation.

pVT Experimental Data. Since a knowledge of the relation between pressure, volume, and temperature is so useful in calculating the other properties of a gas, extensive measurements of these variables have been made and are to be found in the literature for a number of the common industrial gases. The values obtained are tabulated in a number of arrangements. The volume may be given at a number of combinations of temperature and pressure, or the pressure may be given at a number of combinations of temperature and volume. A convenient arrangement is to tabulate the product of pressure and volume at regular intervals of

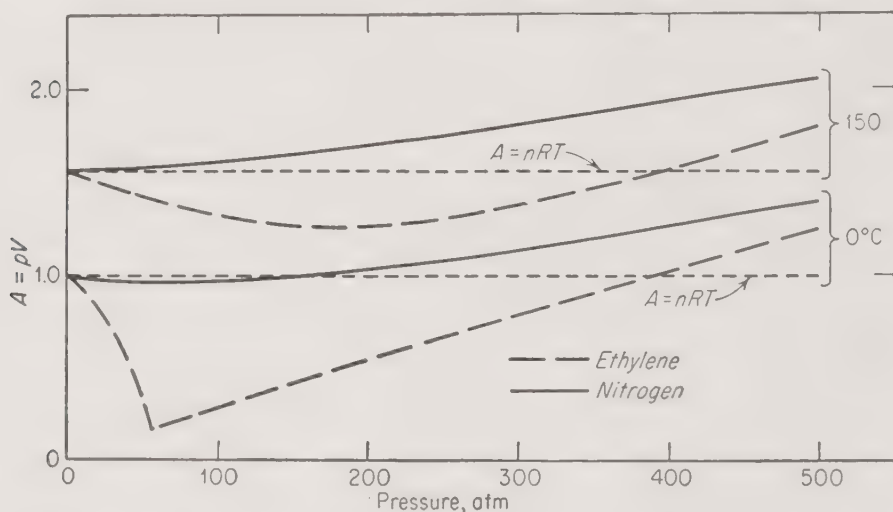


FIG. 8-4. pV curves at constant temperature for two pure substances.

temperature and pressure. When this arrangement is used, it is common practice to choose a basis for each gas such that the product of pressure and volume is unity at 1 atm and 0°C. In order to find the actual volume of a given mass of gas from a table of such pressure-volume products, it is necessary to know the density of the gas at 1.0 atm and 0°C. The product is actually $pV/p_s V_s = A$. When the units for pressure are atmospheres and V_s is unity, $A = pV$. A is termed a compressibility factor. There is also another compressibility factor z defined in the next paragraph.

When the gas is a perfect gas, $A = pV = nRT$, and a graph of A vs. p at constant temperature shows a series of horizontal straight lines, each for a separate temperature, as shown in Fig. 8-4. For an actual gas, these lines deviate considerably from horizontal straight lines. By plotting pV/nRT vs. p , a perfect gas may be represented by a single horizontal straight line which has a value of unity for all temperatures and

pressures. The compressibility factor z is defined as

$$z = \frac{pV}{nRT} \quad (8-2)$$

and z is always unity for a perfect gas.

When z is plotted vs. p for actual gases at several constant temperatures, a series of lines is obtained which converge to unity at low pressures as shown in Fig. 8-5. These lines show different degrees of divergence from unity depending on the temperature and pressure. At lower temperatures, z becomes less than unity as the pressure is increased, indicating that the volume of the gas is less than the perfect-gas volume.

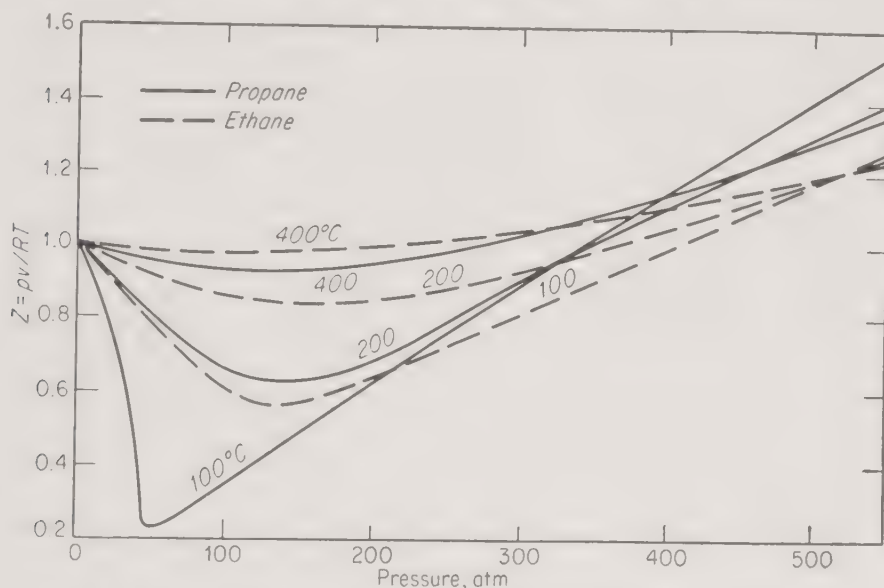


FIG. 8-5. Compressibility factor vs. pressure for two pure substances.

As the pressure is increased further, the volume again approaches the perfect-gas volume and eventually becomes larger. At sufficiently high temperatures, the volume is greater than the perfect-gas volume at all pressures. At higher temperatures, z becomes greater than unity as the pressure is increased from a low value. The temperature at which the compressibility factor z , at low pressures approaching zero as a limit, changes from less than unity to greater than unity is known as the Boyle point. The constant-temperature lines for z vs. pressure do not coincide for different gases but may differ by large amounts as shown on Fig. 8-5. They have somewhat similar general shapes, however, and may be made to coincide more or less closely for all gases by using a relative temperature and a relative pressure. This will be described later.

In using tabulated pVT data as a basis for the calculation of other properties, differentiations, integrations, and other mathematical manipu-

lations are performed on the data. The labor involved in these calculations can frequently be reduced if some thought is given to arranging the calculations to permit use of the data in the form in which they are tabulated.

A number of methods will be described for calculating other properties from pVT data. These are both analytical-mathematical and graphical methods. There are simple, approximate methods of limited accuracy and more detailed procedures that utilize the full precision of the available experimental measurements. These procedures may also be applied to pVT data predicted from generalized correlations in the absence of actual measurements. When so used, they will be limited by the lower accuracy of the data predicted from the correlations.

8-2. Equations of State. The direct analytical-mathematical methods require a mathematical equation for the relation between pressure, volume, and temperature. Such an equation is termed an equation of state. A number of such equations have been developed. Six of these will be discussed and their limitations indicated. These equations may be classified in several ways: according to the number of empirical constants they contain; according to whether they have been constructed from reasoning based on the kinetic theory of gases, on statistical mechanics, on thermodynamics, or on some other principle; or according to whether they are intended for use at low pressures to obtain rough estimates, for engineering calculations over greater pressure ranges, or to represent experimental measurements with the greatest possible precision. The number of empirical constants may range from none to eight or nine or even more. Equations with two constants have been useful in engineering calculations and also serve for a precise representation of measured values when used with an appropriate deviation function. This use will be explained later. Equations are written in forms explicit in p , v , pv , or z . A form of equation of state used in statistical mechanics expresses the compressibility factor z as a series function as follows:

$$\frac{pv}{RT} = z = 1 + \frac{\beta}{v} + \frac{\gamma}{v^2} + \dots \quad (8-3)$$

This is the "virial" form of equation, and β and γ are called the second virial coefficient and the third virial coefficient, respectively. The first virial coefficient is unity and is sufficient to represent the ideal behavior of a gas at infinite molal volume or zero pressure. Both β and γ are functions of temperature but are independent of pressure or density.

Perfect-gas Law. The familiar perfect-gas law

$$pV = nRT \quad (8-4)$$

is the simplest form of an equation of state. It represents the behavior

of gases at low pressures and also in some ranges at higher pressures when the temperature is considerably above the critical temperature. In the regions near the saturation curve, in the vicinity of the critical, and at high pressures it deviates widely from the actual behavior of gases. It contains no empirical constants and cannot be adjusted for variation in behavior from one gas to another.

Van der Waals' Equation. One of the first equations which represents the actual behavior of gases over much wider ranges of pressure, volume, and temperature was proposed by van der Waals,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (8-5)$$

which uses the two constants a and b . Values of these constants for the common gases are given in Appendix C. The constant b represents approximately the volume occupied by the molecules themselves. The constant a is related to the attractive forces between the molecules. The perfect-gas law makes no allowance for the effect of these attractive forces on the pressure exerted by the gas against its container walls. As the gas molecules are crowded together at small specific volumes, these forces become appreciable and the deviations from the perfect-gas law are great. This will be better understood if one will consider an infinitely thin plane in a volume of gas at uniform pressure and temperature. The movement of the molecules will cause them to strike against both sides of this plane and be reflected. The net effect of this process is a transfer to the plane of twice the component of momentum normal to the plane carried by each of the molecules, since each molecule rebounds with an equal momentum in the opposite direction. This transfer of momentum acts as a pressure which is the same on both sides of the plane and is called the *kinetic pressure*. At

low pressures, where the gas follows the perfect-gas law, the kinetic pressure is the same as the gas pressure on the walls of the container.

As the pressure is increased, the average distance between the molecules becomes less, and they exert an attractive force on one another. In the main body of the gas, these attractive forces act on an individual molecule equally in all directions and, on the average, counterbalance one another. This is shown by the molecule on the left side of Fig. 8-6, where the circle around it represents the boundaries of the sphere of action of the inter-

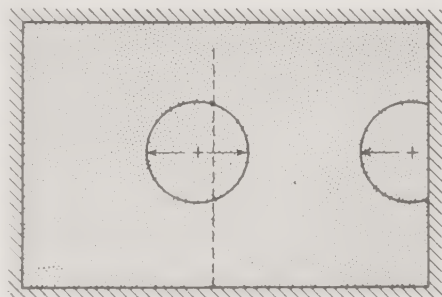


FIG. 8-6. Sphere of action of the intermolecular forces around a molecule near a container wall and at a distance from the wall.

molecular forces. There are as many molecules exerting attractive forces to the right as there are to the left, and the net average force is therefore zero. The same is true at both surfaces of the infinitely thin plane because the molecules on each side act through the plane. The situation is different at the surface of the container wall since there are no gas molecules on the outer side of this surface and thus there are no counterbalancing forces. As a molecule approaches a wall, the unbalanced attractive forces of the other gas molecules act to reduce its velocity, resulting in a gas pressure which is less than the kinetic pressure by an amount which is termed the *internal pressure*, or *cohesive pressure*, I . Thus

$$p = p_k - I \quad (8-6)$$

The van der Waals equation may be rearranged to read

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (8-7)$$

where the first term on the right is p_k and the second term is I .

If both sides of Eq. (8-6) are divided by the pressure p_i of a perfect gas at the temperature T and molal volume v , $p_i = RT/v$, then the ratio p/p_i occurs on the left-hand side and is equal to the difference between the ratio of the kinetic pressure to the perfect-gas pressure and the ratio of the cohesive pressure to the perfect-gas pressure. By definition p/p_i is the compressibility factor z , and then

$$\frac{p}{p_i} = \frac{p_k}{p_i} - \frac{I}{p_i} = z \quad (8-8)$$

The kinetic pressure and cohesive pressure may be determined in a similar fashion from other equations of state.

The isotherm for the critical temperature must have a slope of zero and also show a point of inflection at the critical pressure; therefore, by differentiating Eq. (8-7),

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0 = \frac{-RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} \quad (8-9)$$

$$\text{and} \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = 0 = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} \quad (8-10)$$

Combining Eqs. (8-7), (8-9), and (8-10),

$$v_c = 3b \quad (8-11)$$

$$T_c = \frac{8a}{27Rb} \quad (8-12)$$

$$p_c = \frac{a}{27b^2} \quad (8-13)$$

The constants a and b may be determined from measured values of T_c and p_c by using the following equations,

$$a = \frac{27R^2T_c^2}{64p_c} \quad (8-14)$$

$$b = \frac{RT_c}{8p_c} \quad (8-15)$$

and also
$$\frac{p_c v_c}{RT_c} = 3/8 \quad (8-16)$$

The van der Waals equation predicts the behavior of real gases over rather wide ranges of pressure, volume, and temperature much more closely than does the perfect-gas law, but it too is quite inaccurate, especially near the critical region.

Redlich and Kwong Equation. An equation of state containing only two arbitrary constants cannot be expected to reproduce the behavior of a gas over moderate ranges of pressure and density with an accuracy approaching that of experimental measurements. Equations containing a larger number of constants are used for this purpose. Equations with two constants have great engineering utility if they can be used with moderate accuracy over wide ranges of conditions extending up to pressures of 1,000 atm or more and to high densities. Their utility is enhanced if they can be used to predict or catalog the behavior of mixtures of gases. The equation by Redlich and Kwong² is a two-constant equation with these favorable qualities. It is expressed as

$$p = \frac{RT}{v - b} - \frac{a}{T^{1.25}v(v + b)} \quad (8-17)$$

The constants a and b are determined by the critical temperature T_c and the critical pressure p_c for the pure substance.

$$a = \frac{0.4278R^2T_c^{2.5}}{p_c} \quad (8-18)$$

$$b = \frac{0.0867RT_c}{p_c} \quad (8-19)$$

Equation (8-17) may be expressed in the form

$$z = \frac{pv}{RT} = \frac{1}{1 - h} - \frac{(A^2/B)h}{1 + h} \quad (8-20)$$

Here
$$A = \frac{a^{0.5}}{RT^{1.25}} = \frac{0.6541T_c^{1.25}}{p_c^{0.5}T^{1.25}} \quad (8-21)$$

$$B = \frac{b}{RT} = \frac{0.0867T_c}{p_c T} \quad (8-22)$$

$$h = \frac{Bp}{z} = \frac{b}{v} \quad (8-23)$$

² Otto Redlich and J. N. S. Kwong, *Chem. Revs.*, **44**:233 (1949).

Thus, the two constants a and b , or A^2 and B , are determined from the critical temperature and critical pressure. A^2 and B are constant along an isotherm. The equation has been constructed to be in accord with the behavior of real gases at high pressures. At high pressures, the volume of all gases whose behavior has been observed approaches a limiting value which is practically independent of the temperature. The limiting volume is close to $0.26v_c$, and this value has been assigned to b in order to furnish a good approximation at high pressures.

Berthelot proposed one of the early two-constant equations of state. This is

$$p = \frac{RT}{v - b} - \frac{a}{Tv^2} \quad (8-24)$$

where the two constants a and b are found from

$$a = \frac{27}{64} \frac{R^2 T_c^3}{p_c} \quad (8-25)$$

$$b = \frac{RT_c}{8p_c} \quad (8-26)$$

This equation is known to give a very good approximation at low pressures. Below the critical temperature, the deviation of the Redlich and Kwong equation and of the Berthelot equation from experimental data increases with decreasing temperature. In this temperature range, the Berthelot equation furnishes a better approximation for low pressures.

Enskog Equation. An equation of state developed by Enskog,³ based on the kinetic theory, will be used later in predicting the effect of pressure on the thermal conductivity. This equation relates pressure, density, and temperature.

$$p = \frac{RT}{M} \rho (1 + b\rho X) - a\rho^2 \quad (8-27)$$

The term X allows for the probability of molecular collisions and increases with density. The equation is somewhat similar to van der Waals' equation. The term $b\rho X$ may be treated as a single variable and evaluated from pVT data from the equation

$$b\rho X = \frac{M}{R\rho} \left(\frac{\partial p}{\partial T} \right)_\rho - 1 \quad (8-28)$$

Beattie-Bridgeman Equation. An equation by Beattie and Bridgeman⁴ has found wide application because of the precision with which it repro-

³ S. Chapman and T. G. Cowling, "Mathematical Theory of Nonuniform Gases," chap. 16, The Macmillan Company, New York, 1939.

⁴ J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**:229-308 (1928); see *J. ACS*, **49**:1665 (1927) and **50**:3133 (1928).

duces experimental data. It contains five arbitrary constants, and these are relatively easy to evaluate from a reasonable amount of experimental data. The equation is too cumbersome for approximate engineering calculations but is useful where relatively precise results are necessary. The equation is

$$p = \frac{RT}{v^2} \left[v + B_0 \left(1 - \frac{b}{v} \right) \right] \left(1 - \frac{c}{vT^3} \right) - \frac{A_0}{v^2} \left(1 - \frac{a}{v} \right) \quad (8-29)$$

where B_0 , b , c , A_0 , and a are arbitrary constants. These constants are given in Appendix C for a number of the common gases. The first term on the right of Eq. (8-29) is the kinetic pressure p_k , and the second term is the cohesive pressure I .

The equation was originally applied to 10 gases at pressures up to a maximum of 100 to 200 atm and over a range of densities up to that at the critical. It represented the data for these 10 gases with a precision close to the accuracy of the experimental measurements. However, extrapolation of the equation to pressures above the range where the constants were determined leads to wide deviations from the actual behavior of the gas.

Benedict-Webb-Rubin Equation. The Beattie-Bridgeman equation does not correspond precisely with the pVT properties of substances above their critical density. An equation has been proposed by Benedict, Webb, and Rubin⁵ which may be regarded as a modification of the Beattie-Bridgeman equation to enable it to represent more exactly the properties of fluids at high densities. A single equation of state is used for both gas and liquid phases.

This equation contains eight arbitrary constants and has been applied particularly to hydrocarbons. It has been found to agree with measured pressure-volume-temperature-composition values close to the probable precision of the measurements. The calculation of the isothermal enthalpy and entropy changes with pressure, latent heats of vaporization and mixing, and the fugacities and vapor-liquid equilibria for mixtures has been accomplished from the equation with good agreement with measured values. The equation is

$$p = RTd + \left(B_0RT - A_0 - \frac{C_0}{T^2} \right) d^2 + (bRT - a)d^3 + \alpha \alpha d^6 + \frac{cd^3}{T^2} (1 + \gamma d^2) e^{-\gamma d^2} \quad (8-30)$$

Reference should be made to the original papers for the method of evaluating the eight constants B_0 , A_0 , C_0 , b , a , c , α , and γ .⁶ The evaluation

⁵ M. Benedict, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**:334 (1940); *ibid.*, **10**:747 (1942); also *Chem. Eng. Progr.*, **47**:419 (1951).

⁶ M. Benedict, E. Solomon, and L. C. Rubin, *Ind. Eng. Chem.*, **37**:55 (1945).

of the constants when the equation is used to describe a mixture will be discussed in the section on mixtures. When applied to 12 pure hydrocarbons at densities up to 1.8 times the critical density, the average absolute deviation of gas-phase pressure predicted by the equation from observed values is 0.46 per cent. The average absolute deviation of superatmospheric vapor pressures is 2.1 per cent. Vapor pressures below 1 atm are not predicted with accuracy when using the constants evaluated for the higher pressure range. Better agreement has been obtained by adjusting the constant C_0 at temperatures corresponding to subatmospheric vapor pressures. Values of the eight constants for 12 hydrocarbons are available,⁵ as well as the adjusted values of C_0 (see also Appendix C).

8-3. Theorem of Corresponding States. Changes in pressure and temperature give rise to changes in the molal volume and in numerous other physical and thermodynamic properties of pure substances and of mixtures. At first glance, these changes do not follow a regular pattern, but on more careful analysis a surprising degree of consistency is found. The effect of pressure and temperature on gases is organized into a consistent pattern by the theorem of corresponding states. The application of this theorem leads to predicted behavior which is usually within a few per cent of observed behavior. This theorem is not a precise natural law and should not be expected to yield results comparable to accurate measurements. The theorem states: *All gases, when each is compared at a temperature and pressure that is the same fraction of its critical temperature and critical pressure, have nearly the same compressibility factor, and all deviate from perfect-gas behavior to the same degree. They may thus be considered as in corresponding states.* It will be shown later that other properties of gases also deviate from those of a perfect gas to the same degree, for the several gases, when in a corresponding state.

Measured values of the compressibility factor z for several different gases at the same temperature and pressure will differ greatly. However, compressibility factors will be the same if measured at certain temperatures and pressures that are different for each gas. These different temperatures should be the same fraction of the critical temperatures of the several gases, and the different pressures should be the same fraction of the critical pressures. That is, the ratios of T/T_c are the same for all the gases, and the ratios of p/p_c are also the same. The ratio T/T_c is called the *reduced temperature*, and the ratio p/p_c is called the *reduced pressure*. Thus, when each of the several gases is at the same reduced temperature and each is subjected to the same reduced pressure, all will have the same value of z . Since T_c and p_c are different for each gas, the temperature T and pressure p to which each is exposed will be different.

According to the van der Waals statement of the theorem of corre-

sponding states, conditions and properties of all gases should be the same when compared at equal fractions of the conditions and properties at the critical. Accordingly

$$f(p_R, T_R, v_R) = 0 \quad (8-31)$$

Su⁷ makes a distinction between the conditions (e.g., temperature and pressure) and the properties of the gas (e.g., molal volume or density and compressibility coefficient). Corresponding states are identified as having the same reduced temperature and reduced pressure. The properties then bear a unique relationship to the properties of a perfect gas (not the properties at critical conditions) under the same (corresponding-state) conditions. Thus a better approximation than Eq. (8-31) is given by the relation

$$z = f(p_R, T_R) \quad (8-32)$$

Note again that $z = p/p_i$ and is the ratio of the measured pressure to the pressure of a perfect gas at the same temperature and volume as the actual gas. Also $z = v/v_i$ and is the ratio of the measured volume to the volume of a perfect gas at the same temperature and pressure as the actual gas. Su introduced an ideal reduced volume v'_R which is defined as

$$v'_R = \frac{v}{RT_c/p_c} = \frac{zRT/p}{RT_c/p_c} = z \frac{T_R}{p_R} \quad (8-33)$$

and represents the ratio of the measured volume to the volume of an ideal gas at the critical temperature and critical pressure of the actual gas. z may be expressed as a function of the ideal reduced volume. Thus

$$z = f(p_R, T_R) = f_1(p_R, v'_R) = f_2(v'_R, T_R) \quad (8-34)$$

Graphs of the compressibility factor vs. p_R and T_R were first prepared by Cope, Lewis, and Weber⁸ and Brown, Souders, and Smith⁹ for hydrocarbons, and they were later extended by Dodge¹⁰ to include other gases. The average deviation of the compressibility factors compared to the experimental values in 263 cases covering all ranges with 18 different gases was a little under 2 per cent.¹⁰ Ammonia showed the greatest deviation, 15 per cent, but the average for this gas was 7 per cent. The pVT properties of many additional gases have been measured since these earlier charts were prepared. Recently Nelson and Obert¹¹ have prepared new charts based on a survey of 30 gases as reported in a bibli-

⁷ G. J. Su, *Ind. Eng. Chem.*, **38**:803 (1946).

⁸ J. Q. Cope, W. K. Lewis, and H. C. Weber, *Ind. Eng. Chem.*, **23**:887 (1931).

⁹ G. G. Brown, M. Souders, and R. L. Smith, *Ind. Eng. Chem.*, **24**:513 (1932).

¹⁰ B. F. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., 1944.

¹¹ L. C. Nelson and E. F. Obert, *Mech. Eng.*, **76**:280 (1954).

ography of 275 items. Three charts were prepared for the low-pressure region p_R from 0 to 1, the intermediate-pressure region p_R from 0 to 10, and the high-pressure region p_R from 0 to 40.

The chart for the low-pressure region is shown in Fig. 8-7. This has a deviation of 1 per cent for 26 of the 30 gases. The other four gases were hydrogen, helium, ammonia, and water vapor.

In using the theorem of corresponding states, it is necessary to make an allowance for the low-molecular-weight gases hydrogen, helium, and neon which differ somewhat in their behavior from other gases. Newton¹² suggests modifying the definition of reduced temperature and reduced pressure for these gases as follows,

$$T_R = \frac{T}{T_c + 8} \quad p_R = \frac{p}{p_c + 8} \quad (8-35)$$

Hydrogen and helium are brought into agreement with the low-pressure chart by using Newton's correction at or above the Boyle-point isotherm. The Boyle-point isotherm may be considered to be the $z = 1.00$ coordinate with a probable accuracy of 0.004 units. Below the Boyle-point isotherm, better correlation for these two gases is obtained by using the uncorrected reduced temperature and reduced pressure. Ammonia and water show deviations of the order of $2\frac{1}{2}$ per cent. The region of $T_R = 5$ gives maximum values of z . At higher values of T_R the isotherms show decreasing values of z . For example, the isotherms for $T_R = 3$ and $T_R = 15$ closely coincide.

The chart for the intermediate pressure range is shown in Fig. 8-8 and is also based on 30 gases. The maximum deviation for 26 of these gases was $2\frac{1}{2}$ per cent (except near the critical region). Hydrogen, helium, ammonia, and methyl fluoride deviated to a greater extent than this. Ammonia was the most serious and could not be correlated on this chart above $p_R = 1.0$. Methyl fluoride was within $2\frac{1}{2}$ per cent above $T_R = 1.3$ but deviated as much as 7 per cent at lower temperatures. Hydrogen and helium were erratic below the Boyle-point isotherm but were correlated by the chart at higher temperatures with the use of Newton's corrections.

Figure 8-9 shows the chart for the high-pressure region. This is based on 17 substances, but for only a few of these were measurements available over extensive ranges. In the regions where comparison of several gases could be made ($T_R = 1$ to 3.5 and $p_R = 10$ to 20), the maximum deviation was less than 5 per cent. Above the Boyle point, the Newton correction is used with hydrogen and helium. Below the Boyle point, the correction is not used with these two gases but the maximum devi-

¹² R. H. Newton, *Ind. Eng. Chem.*, **27**:302 (1935).

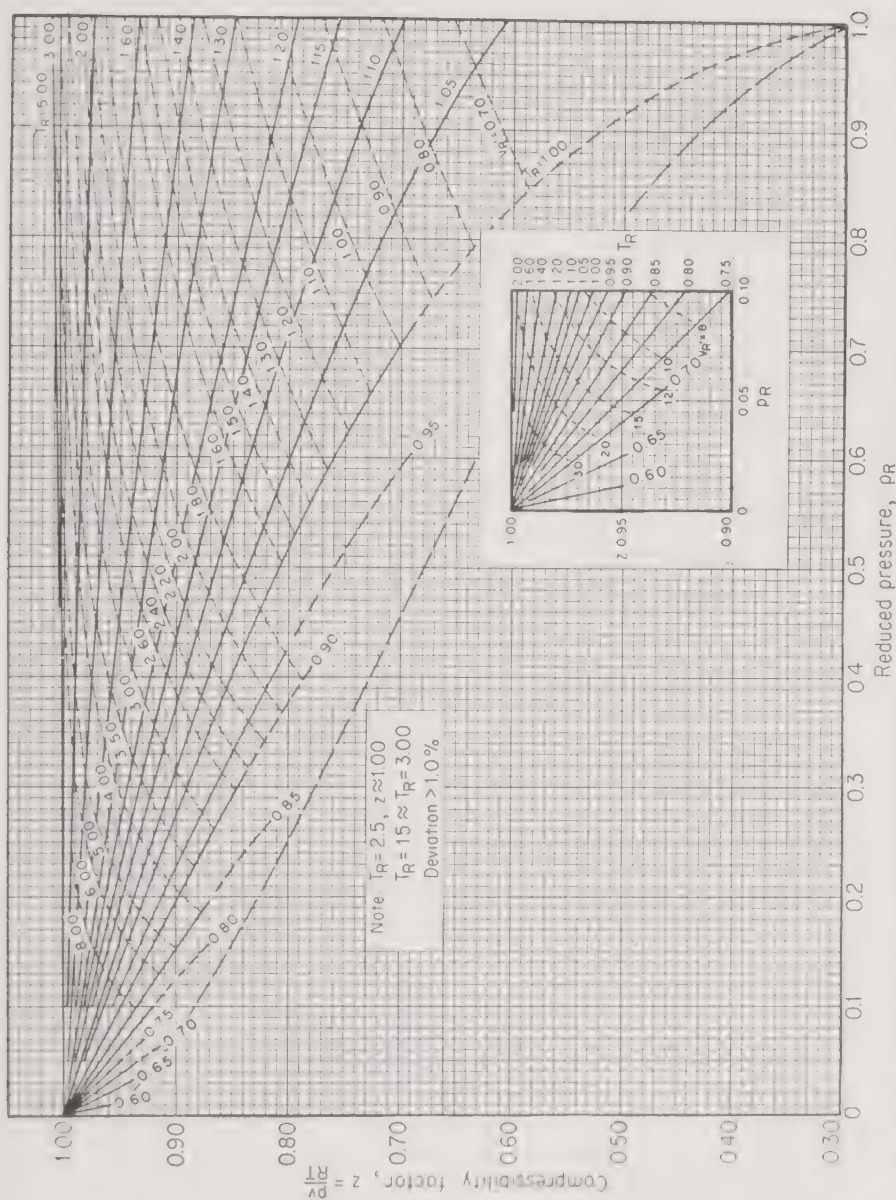


FIG. 8-7. Generalized compressibility-factor chart for low-pressure range. (From L. C. Nelson and E. F. Obert, *Northwestern Technological Institute, Evanston, Ill.*, 1953.)

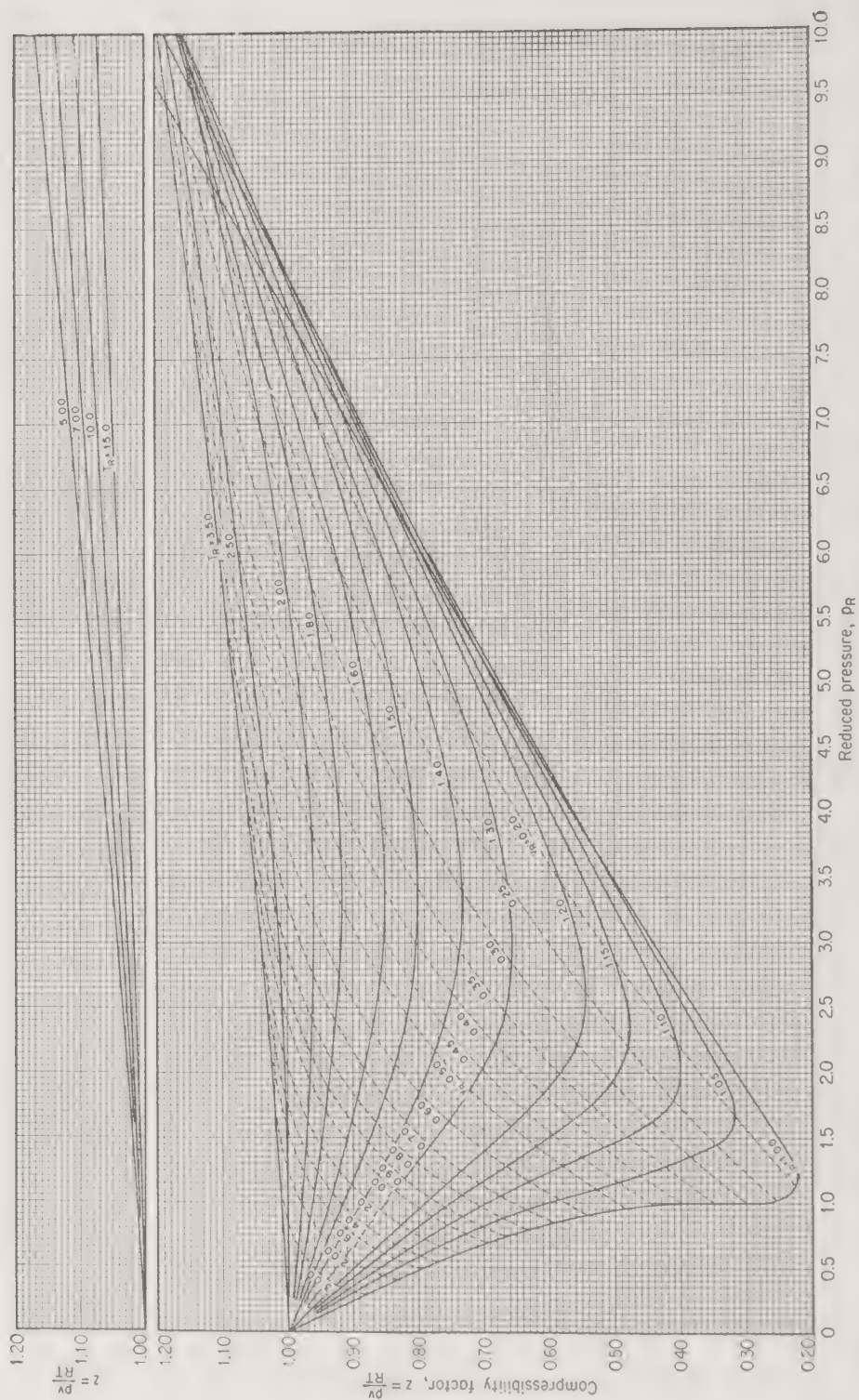


Fig. 8-8. Generalized compressibility-factor chart for intermediate-pressure range. (From L. C. Nelson and E. F. Oberl, *Northwestern Technological Institute, Evanston, Ill.*, 1953.)

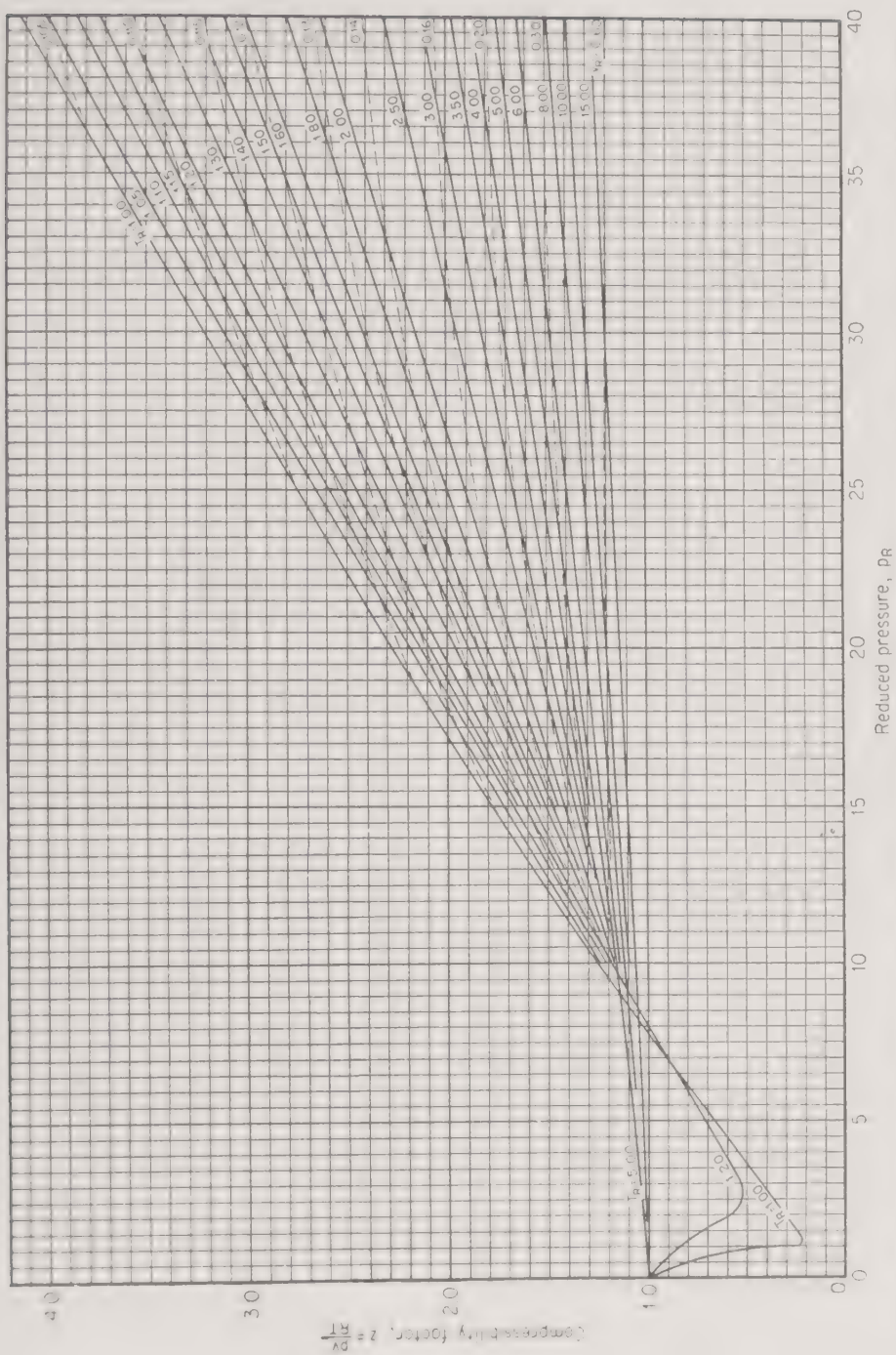


FIG. 8-9. Generalized compressibility-factor chart for high-pressure range. (From L. C. Nelson and E. F. Obert, *Northwestern Technological Institute, Evanston, Ill., 1953.*)

ation is 10 per cent. No data are available for ammonia and methyl fluoride in this region.

The several equations of state and the charts just described are compared by applying them to three gases chosen arbitrarily. Figures 8-10 and 8-11 compare the per cent deviation, based on the experimental values, of the compressibility factors of nitrogen, ammonia, and ethylene, as predicted by the perfect-gas law, van der Waals' equation, the Beattie-Bridgeman equation, the Redlich and Kwong equation, and Figs. 8-7 to 8-9. It is evident that the perfect-gas law deviated to the greatest extent in most cases, although there are small ranges in which it agrees with

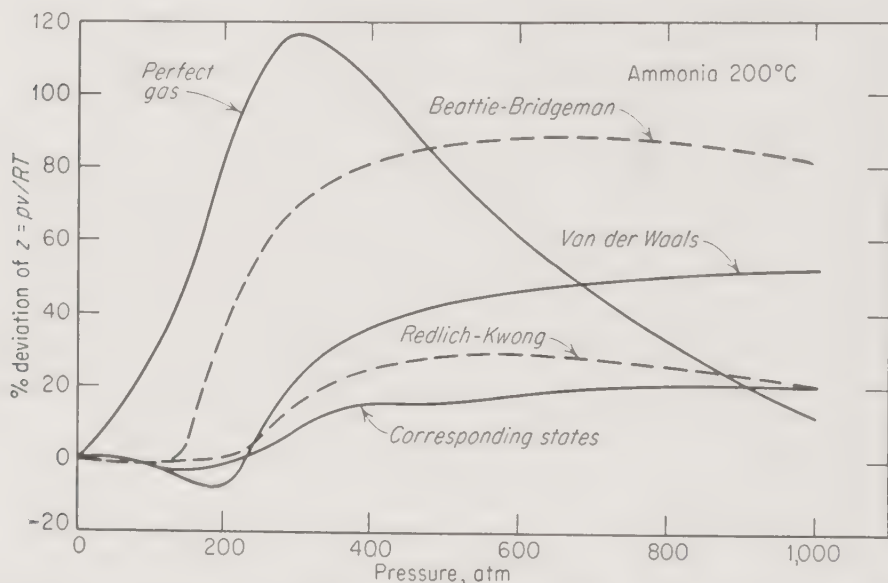


FIG. 8-10. Per cent deviation of the compressibility factor for ammonia from observed measurements.

the measured values better than the other equations. The Beattie-Bridgeman equation is the most accurate over the pressure range up to 100 atm in which the constants used in the equation were evaluated. Extrapolation of this equation to pressures higher than this range may lead to greater deviations than for the van der Waals equation. The values predicted by Figs. 8-7 to 8-9 agree quite well with the experimental data over the entire pressure range.

The theorem of corresponding states is not an exact law, but it serves to predict compressibility factors which are often of sufficient accuracy for engineering calculations and are a great improvement over the perfect-gas law when used at pressures above several atmospheres. It can be shown that the precision of the theorem of corresponding states in reproducing experimental data is limited to that of an equation of state containing two or three arbitrary constants in addition to the gas constant R .

No equation with three constants has yet been found to represent the full precision of experimental data for one gas. This reflects the approximate although quite useful nature of the theorem of corresponding states. In applying this theorem, the only information needed about a gas is its critical temperature and critical pressure.

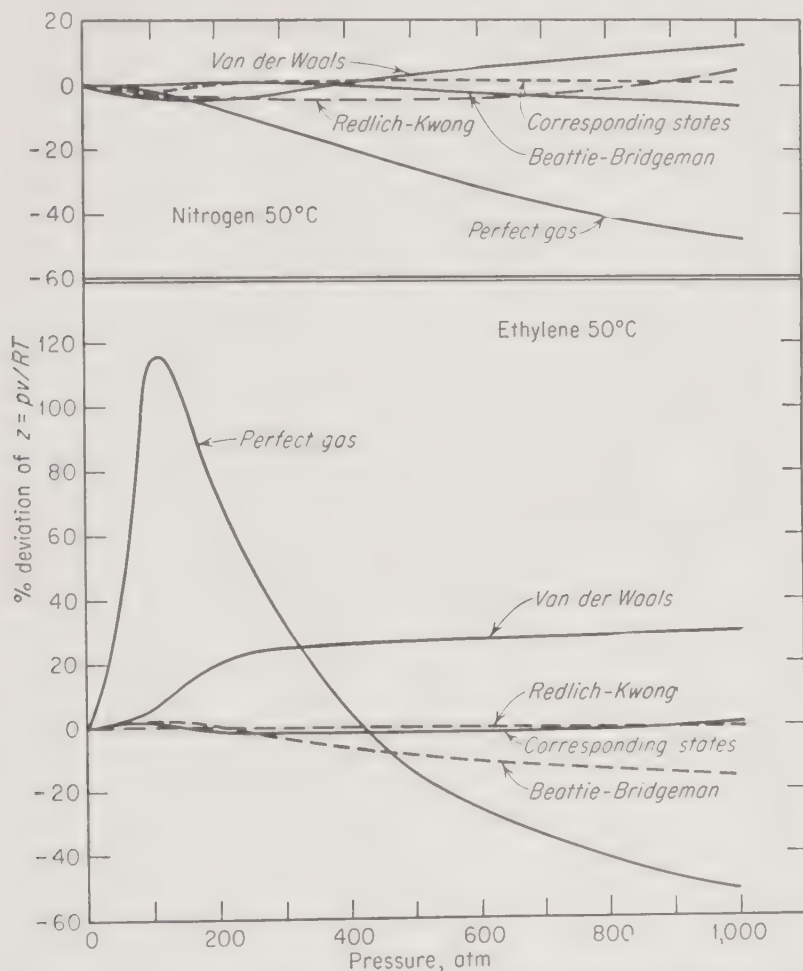


FIG. 8-11. Per cent deviation of the compressibility factor for ethylene and nitrogen from observed measurements.

The theorem of corresponding states may be expanded by adding a third parameter represented by C in a modification of Eq. (8-32).

$$z = f(p_R, T_R, C) \quad (8-32a)$$

Several properties have been proposed for the third parameter. Lydersen, Greenkorn, and Hougen^{12a} have compared the effect of these pro-

^{12a} A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, Generalized Thermodynamic Properties of Pure Fluids, *Univ. Wisc. Eng. Expt. Sta. Rept.* 4, 1955.

posed parameters using pVT data from 82 compounds. On the basis of these comparisons, they conclude that z_c , proposed by Meissner and Seferian,^{12b} is a suitable third parameter. Values of z were then tabulated against p_R and T_R for four values of z_c : 0.23, 0.25, 0.27, and 0.29. These tables are reproduced in Appendix D. Comparison of these tables with the compressibility factors of the 82 compounds shows an average deviation increasing from zero at low pressures up to 2.5 per cent in the critical region and then diminishing to 2.0 per cent at the highest pressures. The tables include values for both gases and liquids but are not applicable to hydrogen and helium in the range of liquefaction. Tables of reduced density are also available^{12a} and are recommended for estimating the density of liquids.

8-4. Calculation of Thermodynamic Properties from pVT Measurements. The pVT measurements may be used to calculate a number of the properties of pure substances. The calculation of these properties at elevated pressure is of particular interest for purposes of engineering design. Several methods of calculation have been employed.

Using an Equation of State. An equation of state may be used to represent the measurements, and this equation can then be subjected to a mathematical treatment in accordance with the laws of thermodynamics. This usually involves differentiating the equation of state and subsequently performing an integration over a range of pressures. This method has been used in the preparation of the steam tables as well as for similar tables of the thermodynamic properties of other substances, such as ammonia and certain refrigerants. When experimental data of high precision are available and the applications for the calculated data warrant the expenditure of time and effort, this method is capable of utilizing the full precision of the measurements. Equations of state with as many as 10 empirical constants have been used to represent experimental results over limited ranges. Approximate values of the properties can be calculated with less effort by using simpler equations. In any case, this method requires an equation of state for the ranges in which calculations are made.

This method has been used by Seifarth and Joffe¹³ to calculate $C_p - C_p^*$, the change in the heat capacity at constant pressure from a low pressure to elevated pressures, for propane. The pVT behavior of propane was expressed by the Benedict-Webb-Rubin equation of state, and, with the aid of well-known thermodynamic relationships, the change in heat capacity was found to be

^{12b} H. P. Meissner and R. Seferian, *Chem. Eng. Progr.*, **47**:579 (1954).

¹³ J. N. Seifarth and J. Joffe, *Ind. Eng. Chem.*, **44**:2894 (1952).

$$C_p - C_p^* = \frac{T \left[R + \frac{B_0 R}{v} + \frac{2C_0}{T^3 v} + \frac{bR}{v^2} - \frac{2C}{v^2 T^3} \left(1 + \frac{\gamma}{v^2} \right) e^{-\gamma/v^2} \right]^2}{RT + \frac{2}{v} \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) + \frac{3}{v^2} (bRT - a) + \frac{6a\alpha}{v^5} + \frac{ce^{-\gamma/v^2}}{v^2 T^2} C_1} \\ + \frac{6C_0}{T^3 v} + \frac{6c}{T^3 \gamma} (e^{-\gamma/v^2} - 1) + \frac{3c}{T^3 v^2} e^{-\gamma/v^2} - R \quad (8-36)$$

where $C_1 = 3 + 3\gamma/v^2 - 2\gamma^2/v^4$. This equation is indicative of the complicated type of calculations required to retain the full precision of the experimental measurements.

Graphical Calculation Using Residuals. A major part of the labor involved in determining the constants of a suitable equation of state may be avoided by making the calculations directly from the experimental values by a graphical method. One soon finds that excessively large graphs are needed to reproduce the precision of the data, and this magnifies errors associated with the distortion of the paper and the construction of long reference lines. A combination of the desirable features of the equation-of-state method and the graphical method of calculation is provided by the use of residuals. In this method, the measured values are fitted approximately by a suitable equation of state, and the quantity required to bring the equation of state into agreement with the smoothed experimental values is termed a residual. These residual values are represented graphically. The calculation consists in using the equation of state in an approximate analytical calculation and correcting the result by a graphical calculation using the residuals. The graphical calculation is thus only a correction to the analytical calculation and need not be of great precision. The charts required are of convenient proportions; the equation of state need not fit the data precisely.

Example 8-1. As an example of the use of residuals, the change with pressure in heat capacity C_p will be calculated. Experimental pVT data on nitrogen are given in the literature¹⁴ as shown in Table 8-1. From these data and the value 6.92 for C_p at 50°C and 1 atm, the value of C_p in cal/(mole)(°C) from 1 to 1,000 atm will be calculated using the method of residuals. From thermodynamics

$$\left(\frac{dC_p}{dp} \right)_T = -T \left(\frac{d^2v}{dT^2} \right)_p \quad (8-37)$$

Integrating this at constant temperature from a low pressure p^* to the pressure p

$$C_p = C_p^* + \int_{p^*}^p -T \left(\frac{d^2v}{dT^2} \right)_p dp \quad (8-38)$$

¹⁴ W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**:638 (1931).

The tabulated data will be represented by the perfect-gas law plus a residual. A convenient residual is defined as

$$\alpha = \frac{RT}{p} - v \tag{8-39}$$

This is the difference between the perfect-gas-law volume at any temperature

TABLE 8-1†

Pres- sure, atm	Temperature, °C						
	-25	0	20	50	100	200	300
	Volume, cc/g						
20	35.75	39.67	42.74	47.33	54.87	69.82	84.64
40	17.65	19.72	21.33	23.72	27.59	35.21	42.70
60	11.66	13.11	14.23	15.87	18.52	23.68	28.73
80	8.694	9.828	10.70	11.97	14.00	17.93	21.75
100	6.950	7.886	8.604	9.639	11.29	14.48	17.57
200	3.645	4.139	4.524	5.078	5.955	7.637	9.230
300	2.704	3.020	3.271	3.640	4.243	5.389	6.467
400	2.287	2.510	2.693	2.967	3.421	4.287	5.098
500	2.046	2.217	2.360	2.572	2.928	3.622	4.277
600	1.890	2.032	2.146	2.320	2.612	3.192	3.735
800	1.695	1.798	1.880	2.010	2.225	2.655	3.060
1,000	1.567	1.650	1.717	1.821	1.994	2.333	2.657
1,100	1.516	1.591	1.654	1.748	1.909	2.217	2.509
1,200	1.473	1.543	1.601	1.688	1.836	2.120	2.387

† W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**:638 (1931).

and pressure and the experimental volume at the same temperature and pressure. By differentiating Eq. (8-39),

$$\left(\frac{d\alpha}{dT}\right)_p = \frac{R}{p} - \left(\frac{dv}{dT}\right)_p \tag{8-40}$$

and, differentiating a second time,

$$\left(\frac{d^2\alpha}{dT^2}\right)_p = -\left(\frac{d^2v}{dT^2}\right)_p \tag{8-41}$$

Therefore, from Eqs. (8-38), (8-39), and (8-41),

$$Cp = C_p^* + T \int_{p^*}^p \left(\frac{d^2\alpha}{dT^2}\right)_p dp \tag{8-42}$$

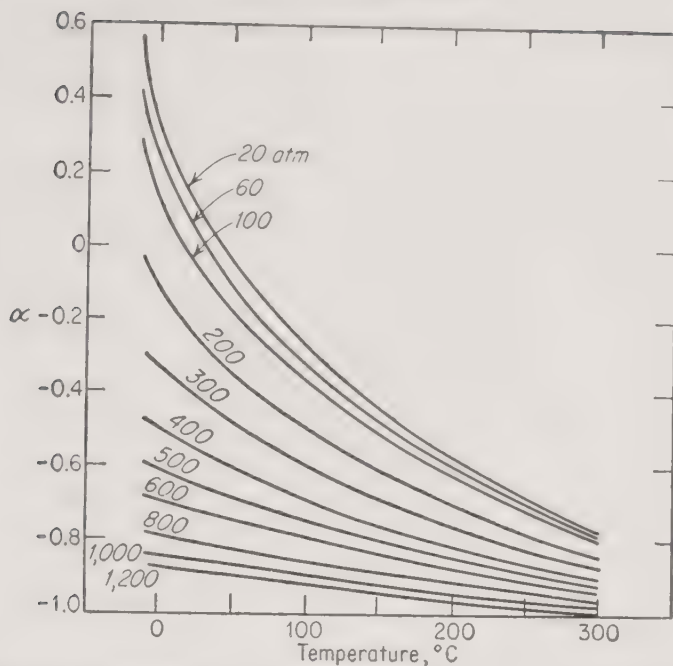


FIG. 8-12. Residual α vs. temperature at constant pressure.

In Fig. 8-12 the values of α calculated from the above table of pVT data are shown plotted vs. temperature at several values of constant pressure. The slope of these curves was measured graphically at 0, 25, 50, 100, and 200°C and is shown in Fig. 8-13 as $-(d\alpha/dT)_p$ vs. temperature at several constant pressures. The slope of these curves was also determined graphically at 50°C, was then multiplied by 323°K, and is shown in Fig. 8-14 as $T(d^2\alpha/dT^2)_p$ vs. pressure at constant temperature. Graphical integration under this curve from zero pressure to several pressures up to 1,000 atm gives the increase in C_p with pressure over this pressure range. The heat capacity at constant pressure as calculated in this way by Deming and Shupe¹⁴ is shown in Fig. 8-15, where it is compared with the values determined experimentally by Mackey and Krase.¹⁵

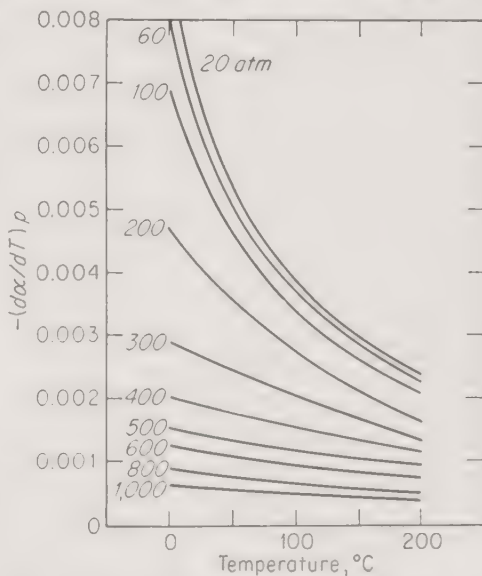


FIG. 8-13. Slope of residual curves vs. temperature at constant pressure.

When the residual as defined by Eq. (8-39) is an appreciable proportion of the measured volume, this method is subject to the same errors

¹⁵ B. H. Mackey and N. W. Krase, *Ind. Eng. Chem.*, **22**:1060 (1930); *J. ACS*, **52**:108 (1930).

as the direct graphical method. York¹⁶ suggests that a second residual in these cases will usually provide the desired exactness. The second

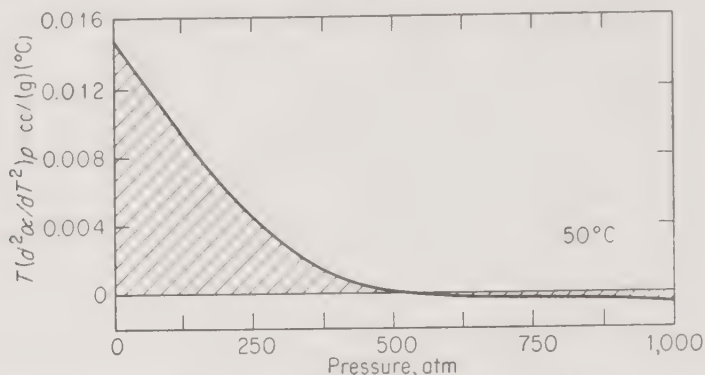


FIG. 8-14. $T(d^2\alpha/dT^2)_p$ vs. pressure for graphical integration.

residual is defined as the difference between the first residual and a simple empirical equation relating the first residual to the independent variable.

Example 8-2. As an example, the second residual will be applied to experimental data for p vs. T at constant volume. The relation between p and T may be expressed approximately by a straight line of the form

$$p' = sT + g \quad (8-43)$$

The first residual r_1 is then defined as the difference between the actual pressure p and p' , or

$$p = sT + g + r_1 \quad (8-44)$$

The calculated values of r_1 may be fitted approximately to an exponential equation of the form

$$r'_1 - a = b(c - T)^n \quad (8-45)$$

FIG. 8-15. Effect of pressure on the heat capacity at constant pressure for nitrogen. [From W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**:638 (1931).]

by plotting $r_1 - a$ vs. $c - T$ on logarithmic coordinate paper. The value of a is the maximum value of the first residual, and c is the temperature at which this maximum occurs. The second residual r_2 is then the difference

$$r_2 = r'_1 - r_1 \quad (8-46)$$

and

$$p = sT + g + a + b(c - T)^n - r_2 \quad (8-47)$$

If, as an example, the data are used to evaluate the derivative $(dp/dT)_v$, then

$$\left(\frac{dp}{dT}\right)_v = s - bn(c - T)^{n-1} - \left(\frac{dr_2}{dT}\right)_v \quad (8-48)$$

¹⁶ R. York, *Ind. Eng. Chem.*, **32**:54 (1940).

and the term $(dr_2/dT)_v$ is the only one which requires the graphical determination of a slope at several points. This is a relatively minor correction factor.

Residuals may also be defined as the difference between a quantity determined by any of a number of equations of state and the measured values. If the equation of state represents the measured values reasonably well, only the first residual will be needed to reproduce the full experimental accuracy of the measurements. Residuals have been based on the van der Waals equation and on the Benedict-Webb-Rubin equation, for example.

The reader is referred to standard textbooks^{10, 17, 18, 19} on thermodynamics for the definition of a number of useful properties such as enthalpy, entropy, free energy, thermodynamic potential, partial molal quantities, fugacity, activity, and the like. Space is not available here to develop and define these concepts adequately. This discussion will assume a reasonable prior familiarity with these terms.

8-5. The Fugacity and Activity of Pure Substances. In the early development of thermodynamic relationships and their application to phase equilibrium and chemical equilibrium, Gibbs²⁰ employed properties such as free energy, entropy, and the thermodynamic potentials. G. N. Lewis²¹ introduced the concepts of fugacity and activity and described their use. These latter functions have been popular and will be used here.

At low pressure, when a vapor or gas behaves as a perfect gas, the isothermal work of compressing a gas from one pressure to another may be expressed simply in terms of the logarithm of the ratio of the two pressures. At elevated pressure, when the gas does not behave as a perfect gas, this simple function of the ratio of pressures does not give the isothermal work of compression. The fugacity is expressed in the same units as pressure and is so defined that the isothermal work of compression of any gas or vapor can be expressed as a function of the logarithm of the ratio of the fugacities at the two pressures. The fugacity concept is also useful in calculating the effect of pressure on the properties of a pure gas or liquid. It will be shown later that it is useful as a criterion of equilibrium in a chemical reaction between more than one

¹⁷ S. Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Company, Inc., New York, 1947.

¹⁸ O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. II—Thermodynamics, John Wiley & Sons, Inc., New York, 1947.

¹⁹ E. A. Guggenheim, "Thermodynamics," 2d ed., Interscience Publishers, Inc., New York, 1950.

²⁰ J. W. Gibbs, "Collected Works," vol. 1—Thermodynamics, Longmans, Green & Co., Inc., New York, 1928.

²¹ G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

component and as a criterion of phase equilibrium with more than one component. It may be employed in a single-component system and provides an easy transition to the treatment of mixtures of two or more components. The concept of fugacity is related to the free energy F which is defined by the equation

$$F = E + pv - TS \quad (8-49)$$

Differentiating this expression,

$$dF = dE + p dv + v dp - T ds - S dT \quad (8-50)$$

$$\text{and since} \quad dE = T dS - p dv \quad (8-51)$$

$$\text{then} \quad dF = v dp - S dT \quad (8-52)$$

$$\text{For an isothermal change, where } dT = 0 \quad dF = v dp \quad (8-53)$$

For the special case when the system consists of a perfect gas, $v = RT/p$, and

$$dF = RT \frac{dp}{p} = RT d \ln p \quad (8-54)$$

The *fugacity* f for a real gas is partially defined by the similar expression

$$dF = v dp = RT d \ln f \quad (8-55)$$

For a change between two states at constant temperature, one at a low pressure and the other at a high pressure, integration gives

$$F - F^* = \int_{p^*}^p v dp = RT \ln \frac{f}{f^*} \quad (8-56)$$

where f^* and p^* may be chosen to correspond to an arbitrary standard state f° and p° . The ratio f/f^* equal to f/f° represents a relative fugacity and is called the *activity*. A value for f° is defined in order to give the fugacity f a definite value in any state. This is done by setting

$$f^\circ = f^* = p^* = p^\circ$$

at a pressure sufficiently low that the substance follows the perfect-gas law. For practical purposes, this pressure need be only as low as 1 atm, or, better, 0.1 atm. Equation (8-54) may be integrated to give the isothermal reversible work of compression when the pressure of a perfect gas is raised from p^* to p . The fugacity is defined in such a way that the same equation gives the isothermal reversible work of compression of an actual gas when fugacity is substituted for pressure.

The integral $\int_{p^*}^p v dp$ may be evaluated for real gases by using a suitable equation of state to relate v and p or by a graphical method based directly on experimental pVT data. This is done as follows:

$$v = \frac{RTz}{p} \quad (8-57)$$

Then, from Eq. (8-55), $d \ln f = z dp/p$. For convenience, the term dp/p may be added and subtracted without altering the equation. Then, for constant temperature,

$$d \ln f = d \ln p + (z - 1) \frac{dp}{p} \quad (8-58)$$

Integrating Eq. (8-58) at constant temperature from the pressure p^* , where p^* approaches zero, to the pressure p results in the equation

$$\ln f - \ln f^* = \ln p - \ln p^* + \int_0^p \frac{z - 1}{p} dp \quad (8-59)$$

At this low pressure $f^* = p^*$, and therefore

$$\ln \frac{f}{p} = \ln \phi = \int_0^p \frac{z - 1}{p} dp \quad (8-60)$$

The integral on the right may be evaluated graphically by measuring the area under a curve derived from experimental data by determining several

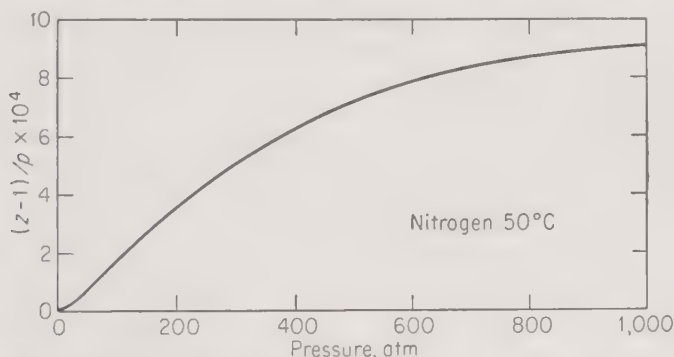


FIG. 8-16. Curve for graphical integration of $(z - 1)/p$ vs. pressure.

values of $(z - 1)/p$ at pressures from 0 to p and making a graph of these as the ordinate vs. p as the abscissa as shown in Fig. 8-16. The ratio f/p is the fugacity coefficient ϕ ,¹⁶ and values of this ratio have been determined both from data on single substances and from generalized correlations applying to all gases. The latter will be discussed in the following text.

The Fugacity Coefficient from Corresponding States. The fugacity coefficient $\phi = f/p$ may be obtained from the compressibility factor given in Figs. 8-7 to 8-9. Inserting the value of $(z - 1)/p$ in Eq. (8-60) and dividing numerator and denominator by p_c results in

$$\ln \phi = \int_0^p (z - 1) \frac{p_c}{p} \frac{dp}{p_c} = \int_0^{p_r} \frac{z - 1}{p_r} dp_r \quad (8-61)$$

It is clear that ϕ will have approximately the same value for any gas when the integral on the right is evaluated along an isotherm at the same value of T_R and up to a pressure with the same value of p_R . In other words, ϕ is very nearly the same for all gases in corresponding states. Several authors have carried out this integration. Newton¹²

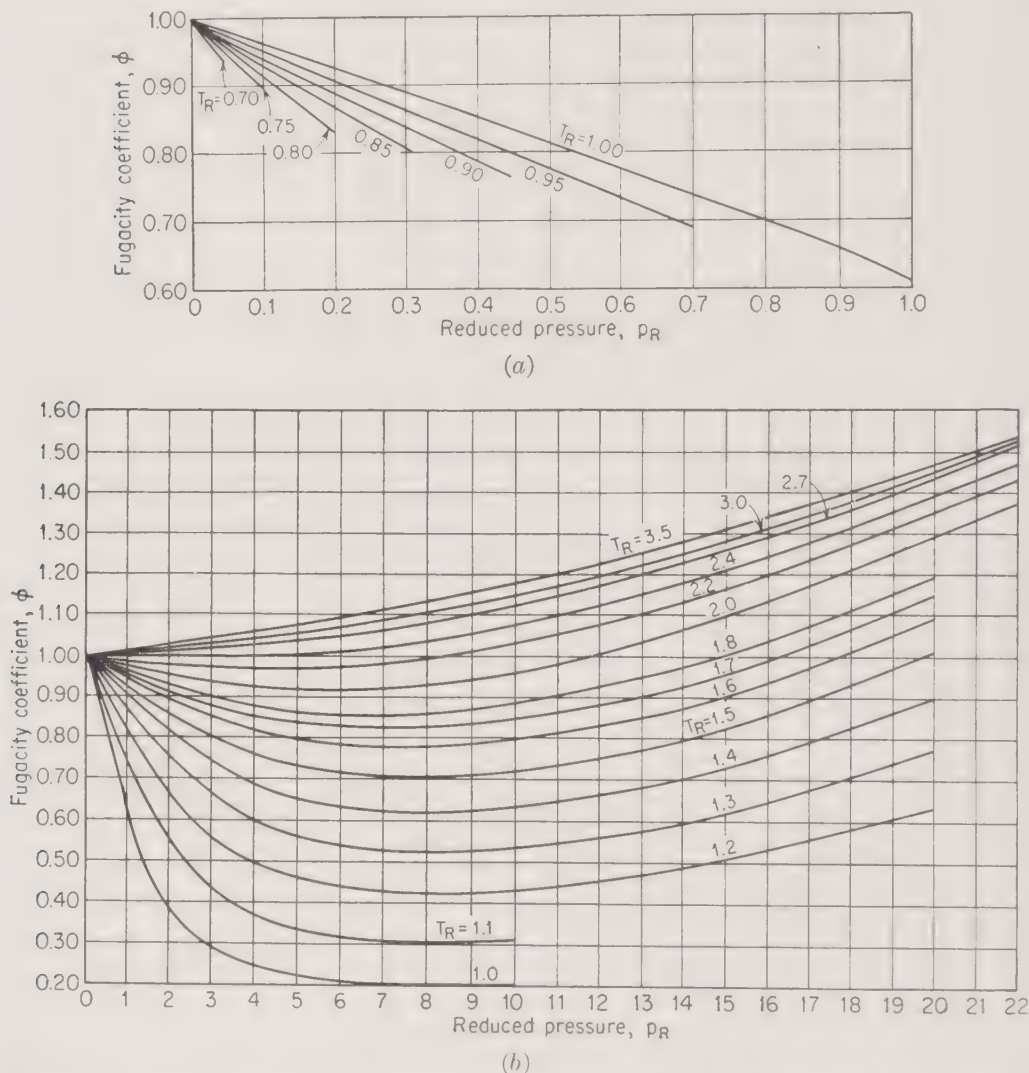


FIG. 8-17. Generalized correlation of fugacity coefficient of gases (a) below the critical temperature, (b) at intermediate temperatures, (c) at high temperatures. [From R. H. Newton, *Ind. Eng. Chem.*, **27**:32 (1935).]

made the graphical integrations based on experimental pVT data and then prepared the generalized charts shown in Fig. 8-17a, b, and c as the average of these calculations. The fugacity coefficient will be found useful in dealing with chemical-reaction equilibrium as well as with the physical equilibrium between phases. Figure 8-17 permits the approximate determination of the fugacity coefficient when accurate pVT data

are not available. Lydersen, Greenkorn, and Hougen^{12a} have prepared tables of fugacity coefficients from their tables of compressibility coefficients.

8-6. Effect of Pressure on Thermodynamic Properties of Gases. Properties such as heat capacity, internal energy, entropy, enthalpy,

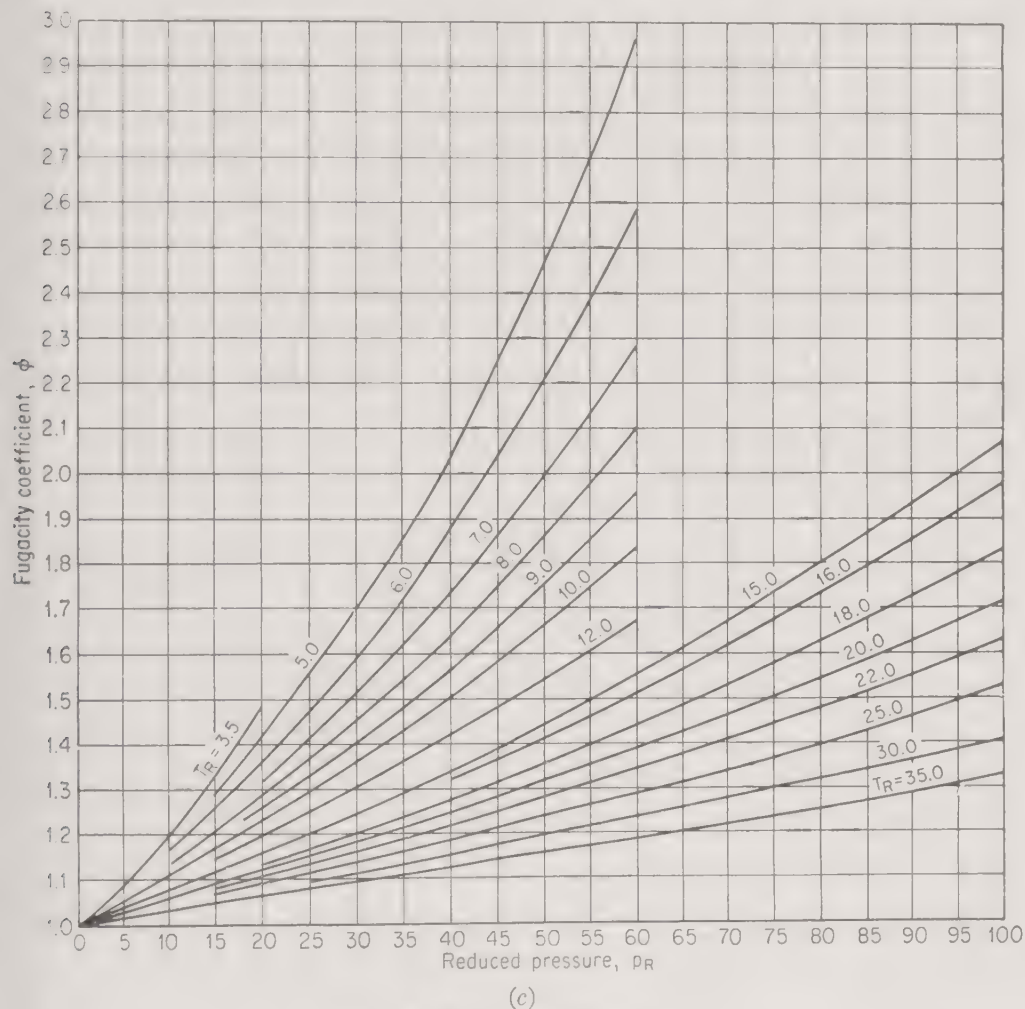


FIG. 8-17. (Continued).

fugacity, and free energy are influenced by pressure. Thermodynamics provides rigorous methods for calculating the effect of pressure on these properties from pVT measurements. These methods may be applied to data in the form of an equation of state or, with less precise but greater general application, to correlations such as those based on the theorem of corresponding states. These latter provide a ready understanding of the magnitude and direction of the effect of pressure.

Consider a gas in state I where its temperature is T and its pressure is p^* with its other properties represented by f^* , H^* , C_p^* , S^* , and the like.

In this state, the pressure is low and the gas follows the perfect-gas law $p^* = f^*$, and H^* is independent of pressure. Now let the gas undergo a change to another state, II, keeping the temperature constant at T but raising the pressure to p . The properties in state II are then f , H , C_p , and S . Rigorous thermodynamic equations are given in textbooks on thermodynamics for calculating the difference between the various properties from state I to state II using pVT data. These may be adapted for use with the compressibility factor, and the results may be put in a generalized graphical form applicable to all gases within the limits of the theorem of corresponding states. This method is used in the following sections.

Enthalpy. The isothermal change in enthalpy with pressure is obtained as follows. The thermodynamic equation for a change in enthalpy is

$$dH = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (8-62)$$

Let $v = zRT/p$, and then, for a constant temperature, $dT = 0$ and

$$T \left(\frac{\partial v}{\partial T} \right)_p = \frac{RT}{p} \left[\frac{\partial(zT)}{\partial T} \right]_p = \frac{zRT}{p} + \frac{RT^2}{p} \left(\frac{\partial z}{\partial T} \right)_p \quad (8-63)$$

$$v - T \left(\frac{\partial v}{\partial T} \right)_p = - \frac{RT^2}{p} \left(\frac{\partial z}{\partial T} \right)_p \quad (8-64)$$

Then combining Eqs. (8-62) and (8-64),

$$\begin{aligned} dH &= -RT^2 \left(\frac{\partial z}{\partial T} \right)_p \frac{dp}{p} = - \frac{RT^2 T_c^2}{T_c^2} \left(\frac{\partial z}{\partial T} \right)_p \frac{p_c}{p_c} \frac{dp}{p} \\ &= -RT_c T_R^2 \left(\frac{\partial z}{\partial T_R} \right)_{p_R} \frac{dp_R}{p_R} \quad \text{at constant temperature} \end{aligned} \quad (8-65)$$

Integrating between p^* and p and between H^* and H at constant temperature,

$$\frac{H^* - H}{T_c} = RT_c^2 \int_0^{p_R} \left(\frac{\partial z}{\partial T_R} \right)_{p_R} \frac{dp_R}{p_R} \quad (8-66)$$

The right-hand side is a function of T_R and p_R only, since z is a function of T_R and p_R . The ratio $(H^* - H)/T_c$ is thus shown to be the same for all gases when in corresponding states. Such a relationship is shown in Figs. 8-18 and 8-19. These figures are from Hougen and Watson.¹⁸ The values read from the charts should be multiplied by a factor φ_1 as proposed by York and Weber²² in the temperature range above $T_r = 1$.

²² R. York and H. C. Weber, *Ind. Eng. Chem.*, **32**:388 (1940).

In this range, there is a systematic variation with the critical temperature of the substance, and the factor φ_1 provides a correction for this

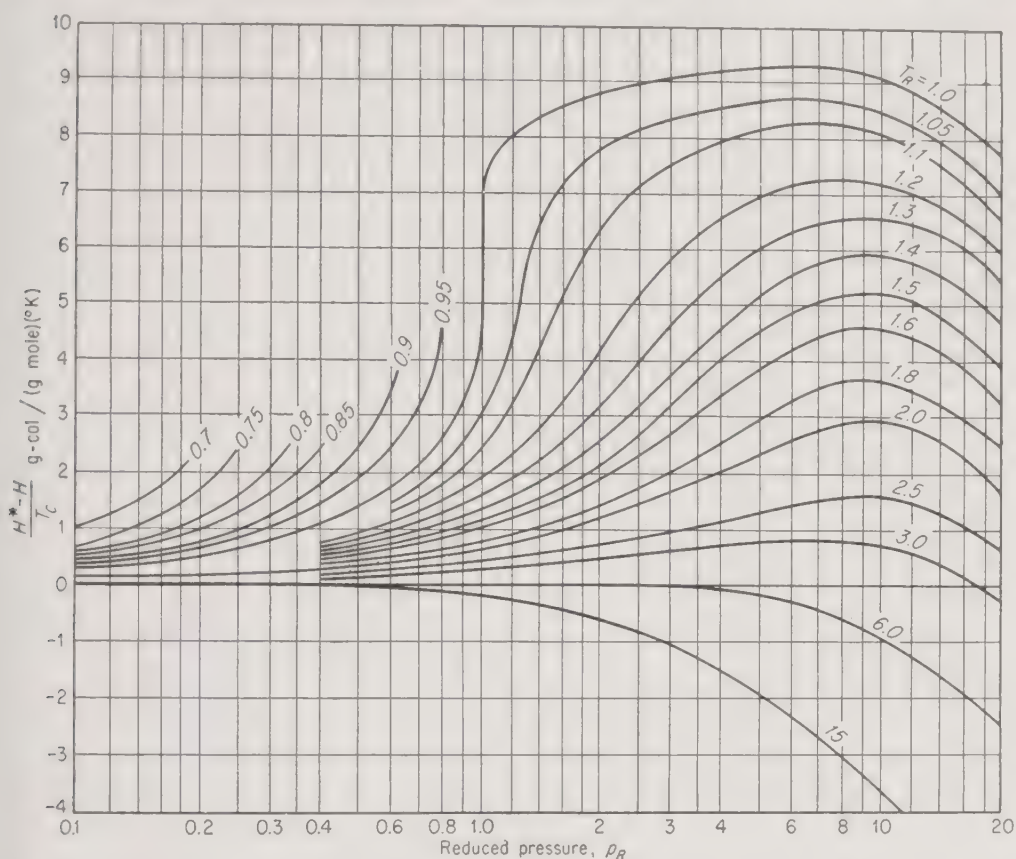


FIG. 8-18. Enthalpy correction for gases (high range). (From O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. II, John Wiley & Sons, Inc., New York, 1947.)

variation. The factor φ_1 is defined as follows,

$$\varphi_1 = \left(\frac{T_c}{470} \right)^n \quad (8-67)$$

where T_c is the critical temperature of the substance in degrees Kelvin and n varies with reduced temperature as shown by the following table:

T_R	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.6
n	0.37	0.28	0.25	0.20	0.18	0.16	0.10	0.14

These charts have been shown to be quite accurate for several hydrocarbons and steam when used with the correction factor φ_1 . This factor has not been evaluated below the critical temperature. However, the

uncorrected values read from Figs. 8-18 and 8-19 are sufficiently accurate for most engineering calculations.

Heat Capacity at Constant Pressure. The variation in this property with pressure has already been calculated for nitrogen. Its variation for other substances may be calculated from the compressibility-factor charts shown in Figs. 8-7 to 8-9. The thermodynamic equation for the iso-

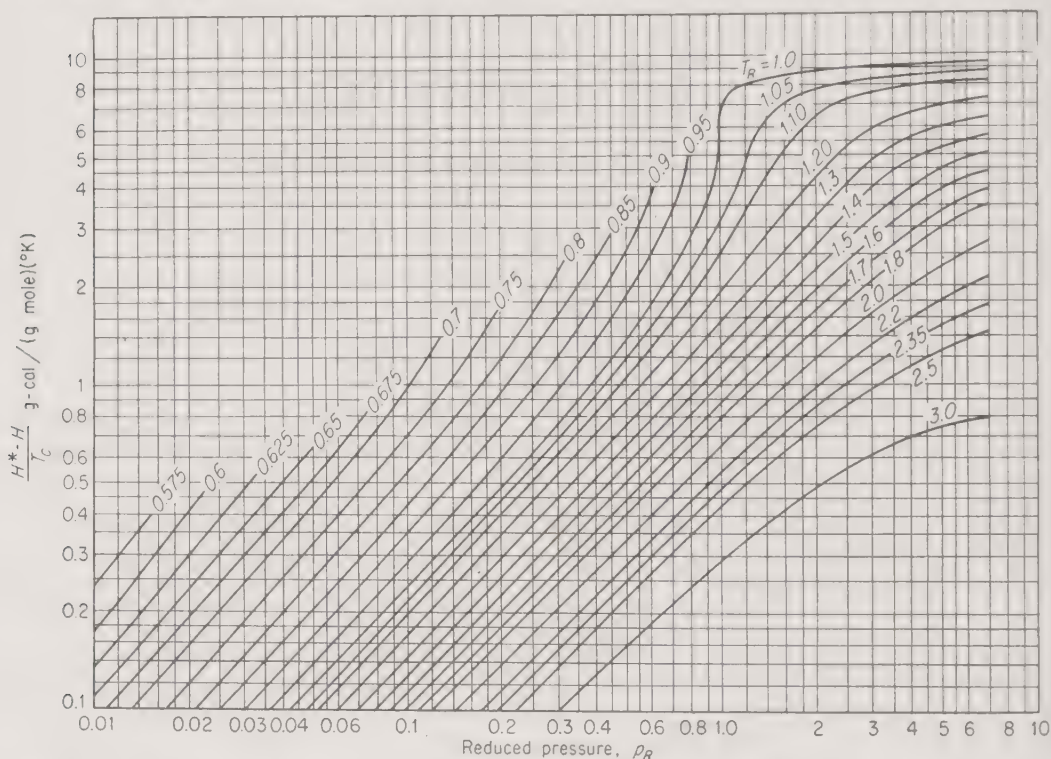


FIG. 8-19. Enthalpy correction for gases (low range). (From O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. II, John Wiley & Sons, Inc., New York, 1947.)

thermal change in heat capacity at constant pressure, when the pressure changes, is again

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_p \quad (8-67)$$

and $v = zRT/p$. Therefore

$$-T \left(\frac{\partial^2 v}{\partial T^2}\right)_p = -\frac{RT}{p} \left[2 \left(\frac{\partial z}{\partial T}\right)_p + T \left(\frac{\partial^2 z}{\partial T^2}\right)_p \right] \quad (8-68)$$

and, since $T = T_c T_R$ and $p = p_c p_R$, integration at constant temperature results in

$$C_p - C_p^* = \int_{C_p^*}^{C_p} dC_p = -RT_R \int_0^{p_R} \left[2 \left(\frac{\partial z}{\partial T_R}\right)_{p_R} + T_R \left(\frac{\partial^2 z}{\partial T_R^2}\right)_{p_R} \right] \frac{dp_R}{p_R} \quad (8-69)$$

showing that $C_p - C_p^*$ is the same for all gases when in corresponding states. Watson and Smith²³ introduced this form of generalized graph. Weiss and Joffe^{23a} have prepared a superior correlation by first calculating $C_p^* - C_p$ for several hydrocarbons and basing the correlation on the calculated values. This is shown in Fig. 8-20. The difference between the heat capacity of a gas at the temperature T and pressure p

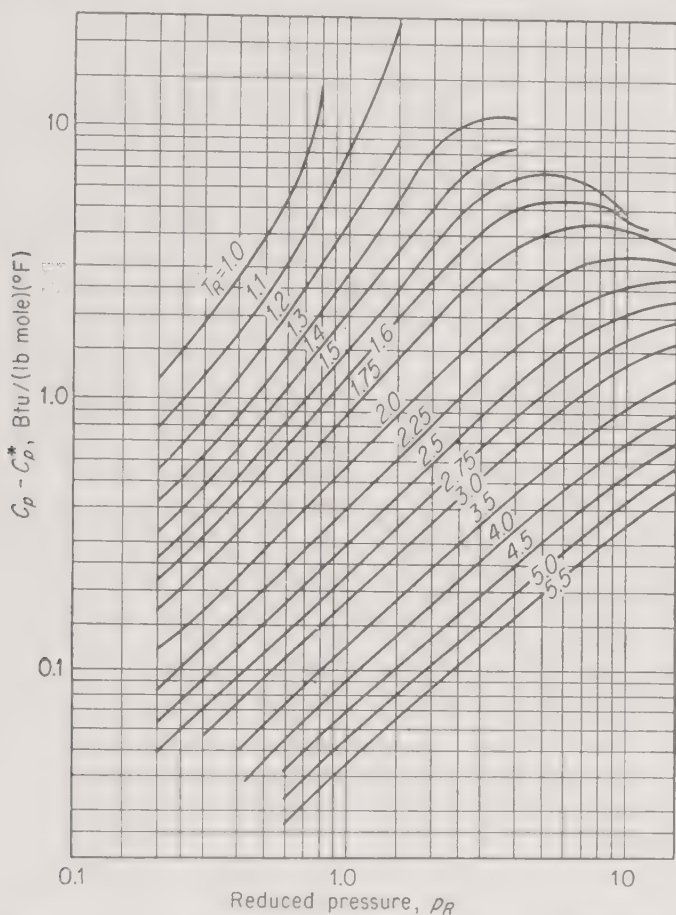


FIG. 8-20. Generalized correlation of $C_p - C_p^*$. [From A. H. Weiss and J. Joffe, *Ind. Eng. Chem.* (to be published).]

and the heat capacity of a perfect gas at the temperature T is shown to be the same for all nonpolar gases when T and p are chosen at the same value of T_R and p_R for each gas.

Energy, Free Energy, and Entropy. By similar thermodynamic reasoning, other thermodynamic properties as shown in Figs. 8-21 and 8-22 may be generalized as follows.

²³ K. M. Watson and R. L. Smith, *Natl. Petroleum News*, July 1 (1936).

^{23a} A. H. Weiss and J. Joffe, *Ind. Eng. Chem.* (to be published).

$$\frac{E^* - E}{T} = R \int_0^{p_R} \left[\left(\frac{\partial z}{\partial \ln T_R} \right)_{p_R} + \left(\frac{\partial z}{\partial \ln p_R} \right)_{T_R} \right] \frac{dp_R}{p_R} = f_1(T_R, p_R) \quad (8-70)$$

$$\frac{F_i - F}{T} = R \int_0^{p_R} \frac{1 - z}{p_R} dp_R = f_2(T_R, p_R) \quad (8-71)$$

where F_i is the free energy of an ideal gas at the pressure corresponding to p_R and at the temperature corresponding to T_R .

$$S_i - S = R \int_0^{p_R} \left[z - 1 + \left(\frac{\partial z}{\partial \ln T_R} \right)_{p_R} \right] \frac{dp_R}{p_R} = f_3(T_R, p_R) \quad (8-72)$$

where S_i is the entropy of an ideal gas at the pressure corresponding to p_R and at the temperature corresponding to T_R . The entropy change $S_i - S$ is shown in Fig. 8-22, and the ratio $(E^* - E)/T$, in Fig. 8-21.

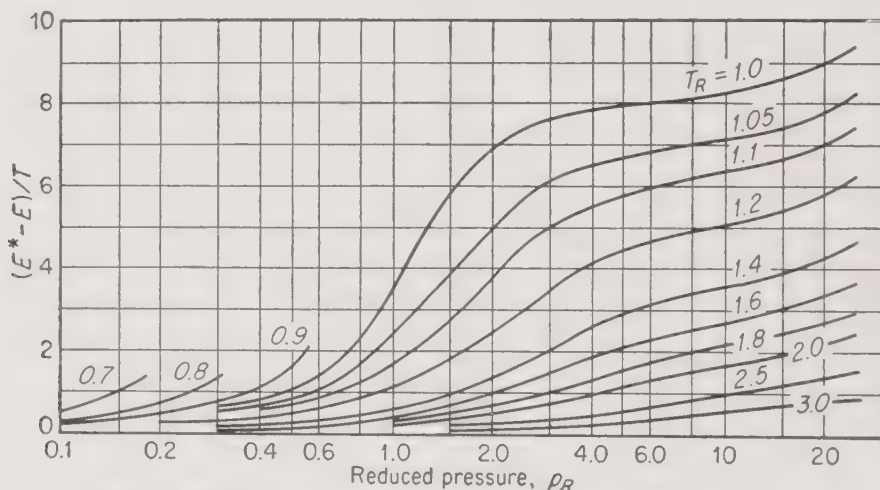


FIG. 8-21. Generalized correlation of $(E^* - E)/T$ vs. p_R .

Lydersen, Greenkorn, and Hougen^{12a} have prepared tables of $(H^* - H)/T_c$, $C_p - C_p^*$, $(E^* - E)/T_c$, and $S_i - S$ each vs. p_R and T_R from their revised tables of compressibility coefficients.

8-7. Compressibility of Liquids. The pVT behavior of a number of liquids has been measured by Bridgman²⁴ and other investigators. The theorem of corresponding states does not apply to the prediction of the properties of liquids as it does to gases, and not so much interest has been shown in predicting the properties of liquids at elevated pressures as has been shown in the case of gases.

Watson²⁵ describes methods for predicting the thermal expansion and the compressibility of liquids, the pressure correction to enthalpy, the

²⁴ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**:185 (1931); *ibid.*, **67**:1 (1932); *ibid.*, **68**:1 (1933).

²⁵ K. M. Watson, *Ind. Eng. Chem.*, **35**:398 (1943).

pressure correction to entropy, the pressure correction to heat capacity at constant pressure, the heat of vaporization, the difference between the heat capacity of a saturated liquid and its ideal gas, and the difference between the heat capacity of the saturated liquid and the heat capacity of the gas at constant pressure. The only data required by his methods are the boiling point, the critical temperature, the critical pressure, and the liquid density at one temperature. His method for predicting the thermal expansion and the compressibility will be described.

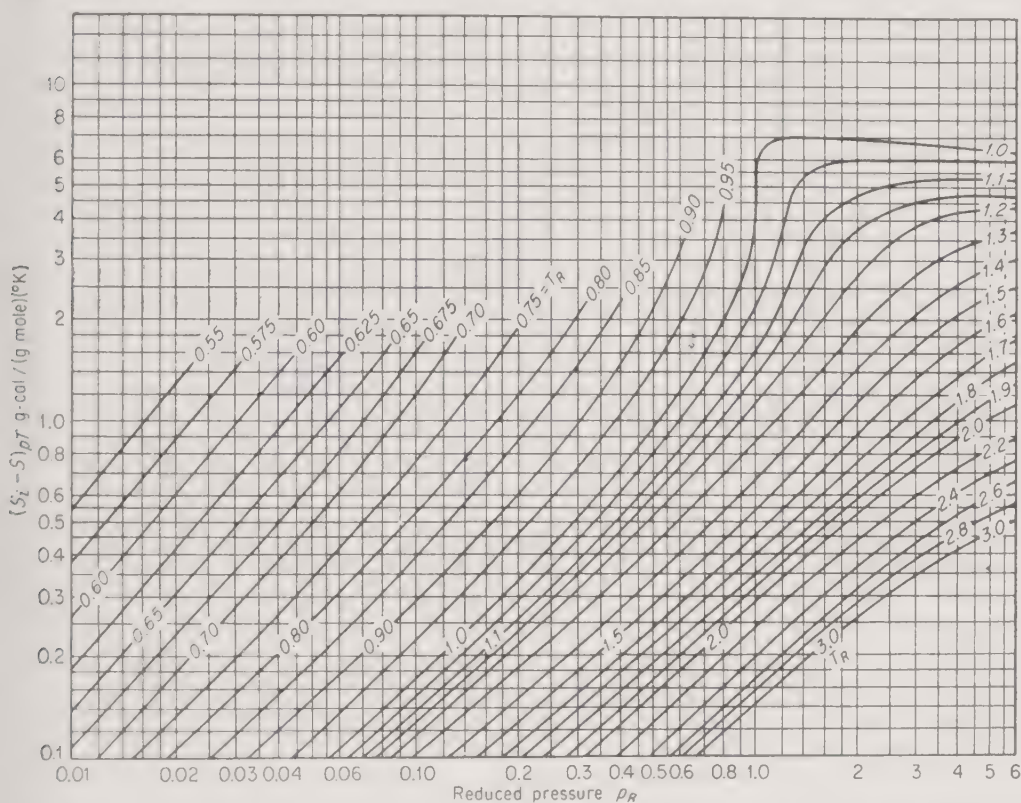


FIG. 8-22. Generalized correlation of $S_i - S$ vs. p_R at constant values of T_R . (From O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. II, John Wiley & Sons, Inc., New York, 1947.)

The equation of state for gases Eq. (8-2) is applied to the liquid state and is rearranged and written as

$$\rho = \frac{pM}{zRT} = \frac{p_R}{zRT_R} \frac{p_c M}{T_c} = \omega \frac{p_c M}{T_c} \quad (8-73)$$

where ω is termed the expansion factor. It is found that ω is not a generalized function of reduced conditions, since at the same reduced conditions values of ω vary as much as 20 per cent for different compounds. A more useful relation employs a measured value of the liquid density for each compound. At least one value of the density is available for a large number of liquids. From Eq. (8-73) it is evident that

ρ/ω is constant for a pure substance, and the equality

$$\frac{\rho}{\rho_1} = \frac{\omega}{\omega_1} \quad (8-74)$$

may be used to predict the density ρ at temperature T and pressure p when the value of ρ_1/ω_1 has been evaluated from the density ρ_1 at T_1

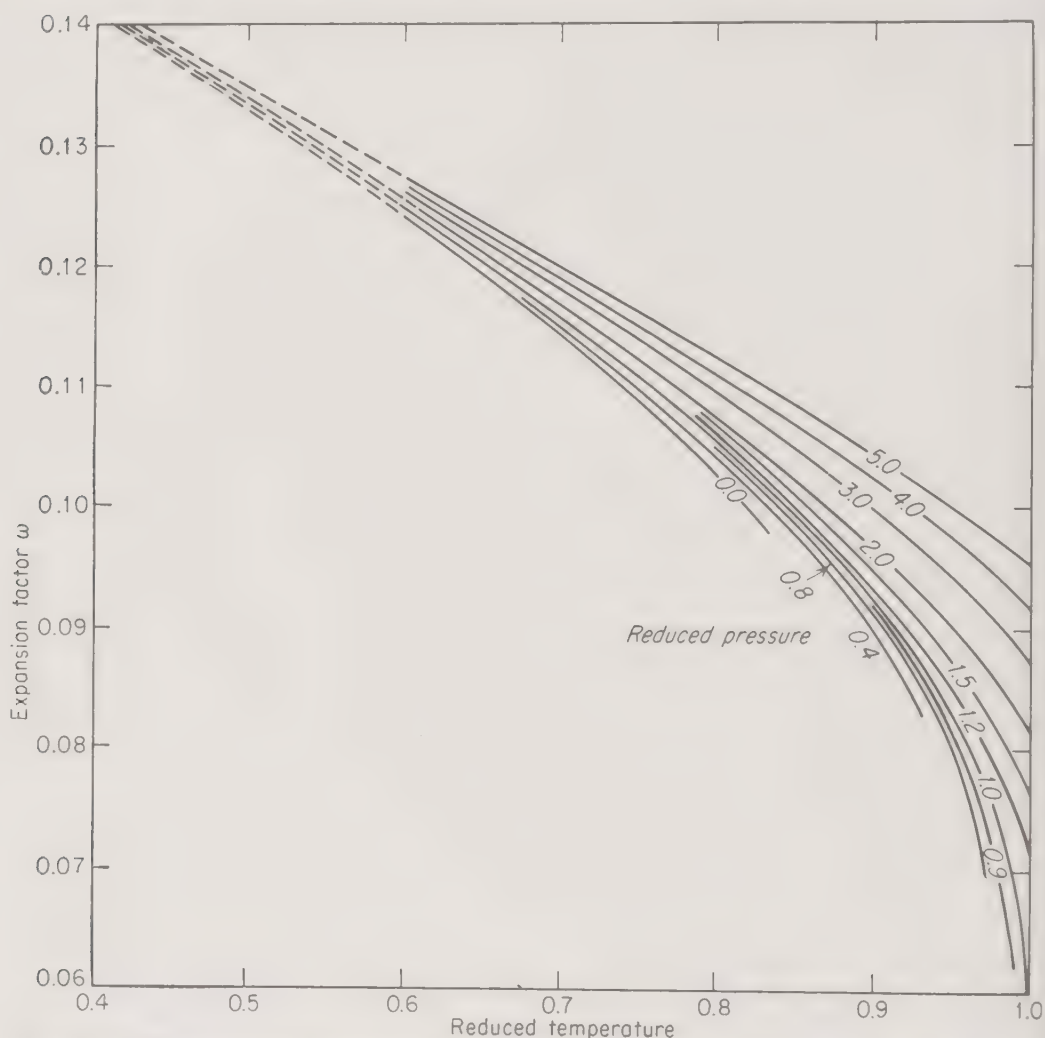


FIG. 8-23. The expansion factor for liquids vs. reduced temperature at constant values of reduced pressure. [From K. M. Watson, *Ind. Eng. Chem.*, **35**:398 (1943).]

and p_1 . It has been found that, when ω is expressed as a function of reduced temperature and reduced pressure for one compound on which complete data are available, it may be used with satisfactory accuracy to predict a value of ω for other liquids, and this may be used in Eq. (8-74) to predict the density. Figure 8-23 gives the values of ω vs. reduced temperature at constant values of reduced pressure based on isopentane and *n*-pentane. Densities were predicted by this method for

water, propane, butane, ammonia, and ethyl alcohol, and deviations from measured values were found to be generally less than 5 per cent. When predicting values in the high temperature range, it is desirable to use a measured value of density at the highest temperature available.

The van der Waals equation of state may be used as a basis for relating the coefficient of thermal expansion or the compressibility of liquids to their boiling point and their heat of vaporization at atmospheric pressure. Wall and Krigbaum,²⁶ using this method of reasoning, observed that

$$\alpha \Delta H_v = 9.4 \text{ cal/}^\circ\text{C} \quad (8-75)$$

$$\text{Here} \quad \alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad (8-76)$$

and ΔH_v is the latent heat of vaporization at the normal boiling point. This relation has been compared with the measured values of 63 organic liquids and found to have an average deviation of ± 0.9 cal/ $^\circ\text{C}$. If the heat of vaporization is known at 25°C , it is better to use this value, but the constant is then 10.1 instead of 9.4 cal/ $^\circ\text{C}$. The product of α and ΔH_v for 37 hydrocarbons at 25°C was found to be quite constant, with an average value of 10.1 ± 0.4 cal/ $^\circ\text{C}$. The value of the coefficient of thermal expansion is particularly useful when a vessel is to be partially filled with liquid at one temperature and then used at a higher temperature. Adequate void space must be allowed to provide for the expansion of the liquid when the temperature is raised. Excessive pressures and bursting of the vessel are likely to result if care is not taken in this regard.

The compressibility is defined as

$$\beta = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad (8-77)$$

Wall and Krigbaum have observed that two relations follow from van der Waals' equation and from Trouton's rule. These are

$$\frac{\Delta H_v^2}{v} \beta = RT \text{ (constant at a given } T) \quad (8-78)$$

$$\text{and} \quad \frac{T_0^2 \beta}{v} = \frac{RT}{C^2} \text{ (constant at a given } T) \quad (8-79)$$

The value of $\Delta H_v^2 \beta / v$ has been determined at 20°C for 42 organic liquids over a pressure range from 100 to 300 atm and was found to be 53.6 ± 3.2 cal²/(ml)(atm). The average value of $T_0^2 \beta / v$ under the same conditions was 0.105 ± 0.007 $^\circ\text{C}^2$ /(ml)(atm). From Eqs. (8-78) and (8-79),

²⁶ F. T. Wall and W. R. Krigbaum, *J. Chem. Phys.*, **17**:1274 (1949).

the values of $\Delta H_v^2/\beta vT$ and $T_0^2\beta/vT$ would be expected to be constant, but sufficient data were not available to substantiate this, and Eqs. (8-78) and (8-79) were thus applied only at 20°C.

Compression of Fluids at Extreme Pressures. At low pressures, where gases behave as perfect gases, their volume varies inversely with the external pressure when the temperature is constant. At higher pressures, the isothermal change in volume with pressure follows more complex relations as shown by the various equations of state which apply in the intermediate pressure ranges. Levitt²⁷ has observed that substances which are gases, liquids, or solids at lower pressures all behave according to the following simple relationship when subjected to extreme pressures,

$$p = Ce^{B/v} \quad (8-80)$$

where B and C are constants characteristic of the particular substance. This is an empirical equation which has been shown to relate the available measurements on four gases, four liquids, four heavy metals, four solid elements, and four solid compounds.

According to this equation, a plot of $\log p$ vs. either $1/v$ or the density ρ is a straight line. This was found to be the case for gases from 1,000 to 15,000 kg/cm², for liquids from 5,000 to 12,000 kg/cm², and for solids from 25,000 to 100,000 kg/cm². By differentiating and rearranging Eq. (8-80), the compressibility β is found to be

$$\beta = -\frac{1}{v} \left(\frac{dv}{dp} \right)_T = \frac{v}{Bp} \quad (8-81)$$

8-8. The Transport Properties. Many of the properties of a fluid are interrelated, and one such property may be calculated if others are known. For the properties of a system in a static or equilibrium state, these calculations are made with the help of thermodynamics, and the properties are known as the thermodynamic properties. Examples of such properties are the energy, the entropy, the enthalpy, and the like. In determining these properties, the system is maintained in a uniform condition with no variation from point to point. There are other properties which are associated with a variation from one point in the system to another. Such variations are called gradients. Viscosity is associated with a velocity gradient, thermal conductivity with a temperature gradient, and molecular diffusivity with a concentration gradient. As a result of such gradients, there is a movement or transport of an entity through the system. A velocity gradient gives rise to transport of momentum, a temperature gradient, to transport of energy, and a concentration gradient, to transport of matter. The viscosity, thermal conductivity,

²⁷ L. S. Levitt, *J. Phys. Chem.*, **58**:573 (1954).

molecular diffusivity, and the like, are called transport properties. Pressure has a pronounced effect on the transport properties, but this effect cannot be calculated by thermodynamic methods as can be done for the thermodynamic properties.

8-9. Viscosity of Gases. Viscosity is primarily associated with a fluid moving in laminar, or noneddying, flow and having a velocity gradient normal to the direction of flow. The coefficient of viscosity is defined as the ratio of the unit shearing stress τ acting at a plane in a fluid to the velocity gradient perpendicular to the plane of shear. This is expressed by

$$\mu = \frac{\tau}{du/dy} \quad (8-82)$$

In a gas flowing in laminar motion, consider a plane parallel to the direction of flow; the number of molecules crossing a unit area of this plane in unit time from one side is the same as the number crossing from the other side. The molecules crossing from one side will possess a greater component of momentum in the direction of flow than those from the other side when a velocity gradient normal to the direction of flow exists. This results in a net transfer of momentum across a unit area of the plane in unit time and indicates that a shear stress is required to maintain the velocity gradient.

It was shown in Sec. 8-2 that the kinetic pressure results from the transfer of molecular momentum. The kinetic pressure differs from the viscosity in that the direction of the momentum being transported is normal to the plane in the case of the kinetic pressure and parallel to the plane for the viscosity. As an increase in pressure causes the kinetic pressure to deviate from the pressure of a perfect gas, so would it be expected to cause the viscosity μ to deviate from the viscosity of a perfect gas μ_i ; and the deviation should be to the same degree,

$$\frac{p_k}{p_i} = \frac{\mu}{\mu_i} \quad (8-83)$$

If this were so, μ/μ_i could be evaluated from pVT data. This relation is valid to a first-order approximation, but Enskog³ has shown that an analysis based on a definite molecular model predicts a moderate difference between the two ratios and yields the following equation for the ratio μ/μ_1 , where μ_i is taken equal to the viscosity at 1 atm μ_1 .

$$\frac{\mu}{\mu_1} = b\rho \left(\frac{1}{b\rho X} + 0.8 + 0.7614b\rho X \right) \quad (8-84)$$

which may be compared to

$$\frac{p_k}{p_i} = 1 + b\rho X \quad (8-85)$$

Equation (8-84) alone cannot be used to predict the ratio μ/μ_1 since both b and $b\rho X$ cannot be evaluated from pVT data alone. The equation is useful in predicting thermal conductivities at high pressures, as will be shown later.

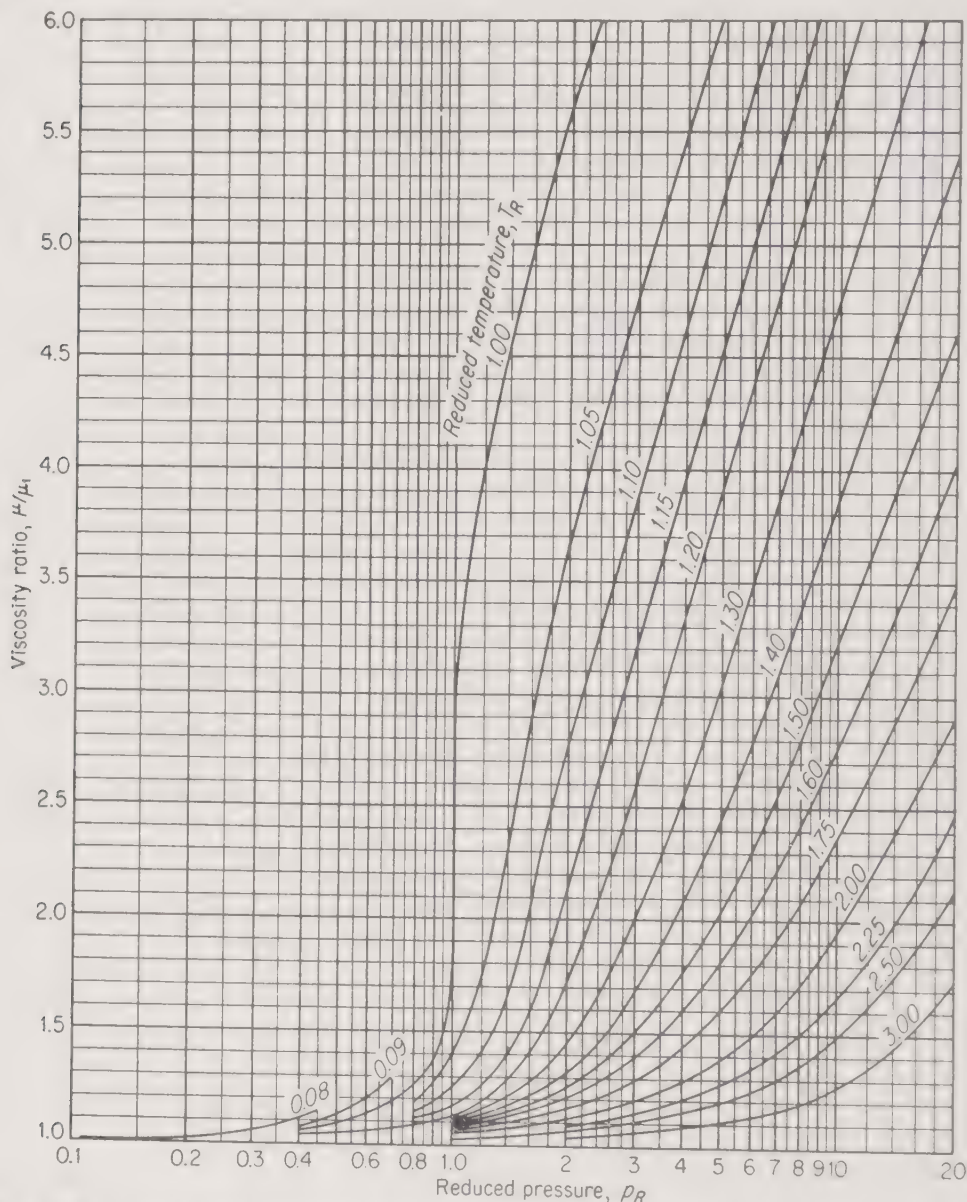


FIG. 8-24. Generalized correlation of the viscosity ratio. [From N. L. Carr, R. Robayaski, and D. B. Burroughs, *Am. Inst. Mining Met. Engrs. Petroleum Technol.*, **6**(10):47 (1954).]

The comparable nature of the compressibility factor z and the viscosity ratio μ/μ_1 as shown by Eqs. (8-8) and (8-83) suggests that μ/μ_1 , like the compressibility factor, will have the same value for all substances in corresponding states. A correlation of μ/μ_1 as a function of the

reduced pressure p_R at several values of the reduced temperature T_R is shown graphically in Fig. 8-24. This type of graphical correlation was originally prepared by Comings, Mayland, and Egly based on carefully chosen experimental data.²⁸ At a reduced temperature and reduced pressure greater than unity, the correlation agrees with experimental measurements within a few per cent in most cases but shows discrepancies of 10 to 12 per cent for ethane at reduced pressures above 2. At reduced temperatures and reduced pressures less than unity, the correlation is not so accurate but is useful for showing general trends. The increase of the viscosity of a gas or vapor with pressure in the range below the critical point is normally less than 50 per cent of the viscosity at atmospheric pressure.

N. L. Carr, R. Kobayashi, and D. B. Burrows²⁹ and N. L. Carr, J. D. Parent, and R. E. Peck³⁰ have shown that recent viscosity measurements on pure hydrocarbons and on mixtures of hydrocarbons agree with the correlation of Comings, Mayland, and Egly and also have extended the graph to higher reduced pressures. Figure 8-24 is their extended correlation. They have shown that the figure may be used for mixtures of hydrocarbon gases by using the pseudocritical temperature and pressure as defined by Kay [see Eqs. (8-110) and (8-111)] in place of the critical temperature and the critical pressure, respectively. The application of this method should be used with caution, since it will give rise to serious inaccuracies for mixtures which are dissimilar chemically or when there is a large difference in the critical temperatures of the components.

Viscosity of Liquids. The viscosity of a liquid, like other liquid properties, does not change so rapidly with an increase in pressure as does the viscosity of a gas. Figure 8-25 shows the effect of pressure on the viscosity of liquid ammonia at several temperatures.³¹ The effect of temperature is more pronounced than the effect of pressure. Nevertheless, at extreme pressures liquids with low viscosity at normal pressures may become highly viscous.

8-10. Thermal Conductivity of Gases. The thermal conductivity k is associated with the transfer of heat in a gas, liquid, or solid from a point at one temperature to another point at a lower temperature. The transfer is from molecule to molecule and not by gross mixing, or convection.

²⁸ E. W. Comings, B. J. Mayland, and R. S. Egly, "The Viscosity of Gases at High Pressures," *Univ. Illinois Eng. Expt. Sta. Bull.* 354 (1944).

²⁹ N. L. Carr, R. Kobayashi, and D. B. Burrows, Petroleum Branch of American Institute of Mining and Metallurgical Engineers, **VI**(10):47 (1954).

³⁰ N. L. Carr, J. D. Parent, and R. E. Peck, *Chem. Eng. Progr. Symposium Ser.* 16, **51**:91 (1955).

³¹ L. T. Carmichael and B. H. Sage, *Ind. Eng. Chem.*, **44**:2728 (1952).

The thermal conductivity is defined as the ratio of the rate of heat transfer per unit area to the temperature gradient in the direction of heat flow, or

$$k = \frac{dq/A \, d\theta}{dt/dx} \quad (8-86)$$

The thermal conductivity of a gas, like the kinetic pressure and viscosity, is one of the transport properties and is associated with the random motion of the molecules. The kinetic pressure and viscosity result from

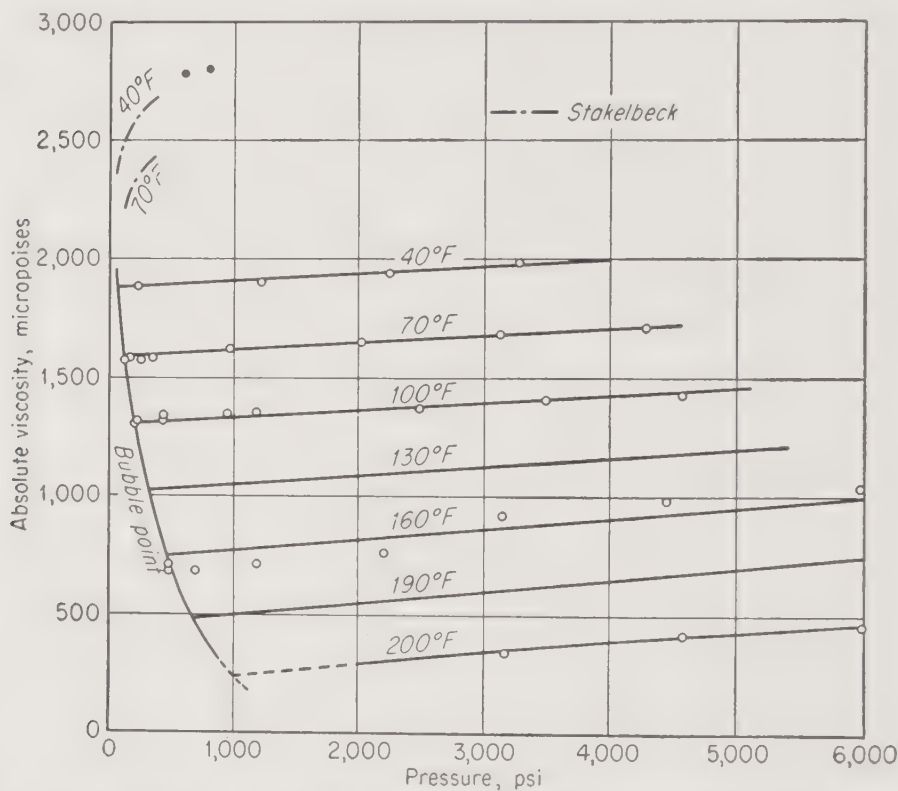


FIG. 8-25. Viscosity of liquid ammonia. [From L. T. Carmichael and B. H. Sage, *Ind. Eng. Chem.*, **44**:2728 (1952).]

the transport of momentum through the gas. The thermal conductivity, on the other hand, results from the transport of energy. It is to be expected that increased pressure will crowd the molecules together, reduce their mean free path, and increase the proportion of the time between collisions that they are within range of the attractive forces from surrounding molecules. The effect of pressure on all properties associated with the molecular transport would be expected to be similar. The effect of pressure on thermal conductivity is quite similar to its effect on viscosity. The equations of Enskog show the small differences between the behavior of these two properties and are useful in predicting the thermal conductivity of compact, spherically symmetrical molecules.

Enskog's equations are three in number and consist of an equation of state relating pressure, density, and temperature,

$$p = \frac{RT\rho}{M} (1 + b\rho X) - a\rho^2 \quad (8-87)$$

an equation relating μ/μ_1 and density,

$$\frac{\mu}{\mu_1} = b\rho \left(\frac{1}{b\rho X} + 0.8 + 0.7614b\rho X \right) \quad (8-84)$$

and an equation relating k/k_1 and density,

$$\frac{k}{k_1} = b\rho \left(\frac{1}{b\rho X} + 1.2 + 0.7574b\rho X \right) \quad (8-88)$$

These three equations may be used to predict values of k/k_1 at any temperature and pressure where pVT data and values of μ/μ_1 are available. By differentiating and rearranging Eq. (8-87),

$$b\rho X = \frac{M}{R\rho} \left(\frac{\partial p}{\partial T} \right)_v - 1 \quad (8-89)$$

and $b\rho X$ may be obtained at any given pressure and temperature from pVT data. Dividing Eq. (8-88) by Eq. (8-84) leads to

$$\frac{k/k_1}{\mu/\mu_1} = \frac{1/b\rho X + 1.2 + 0.7574b\rho X}{1/b\rho X + 0.8 + 0.7614b\rho X} \quad (8-90)$$

It is clear that values of $b\rho X$ and μ/μ_1 are sufficient for the calculation of k/k_1 at the same temperature and pressure. Values of k/k_1 calculated in this manner for the gases whose viscosity and pVT relations are known at higher pressures were correlated³² as a function of reduced pressure and reduced temperature. The calculated values of k/k_1 were larger than the values of μ/μ_1 at the same reduced temperature and reduced pressure by as much as 16 per cent. The measurements of the thermal conductivity of several gases have been used by Lenoir, Junk, and Comings³³ to prepare Fig. 8-26, which is a general correlation of k/k_1 as a function of reduced pressure at several values of reduced temperature. This is similar to Fig. 8-24. Measurements on ethane³³ and propane^{33a} do not agree with this correlation and indicate that the thermal conductivity of nonspherical molecules differs from the uniform behavior suggested by the theorem of corresponding states.

³² L. W. Comings and M. F. Nathan, *Ind. Eng. Chem.*, **39**:964 (1947).

³³ J. M. Lenoir, W. A. Junk, and E. W. Comings, *Chem. Eng. Progr.*, **49**:539 (1953).

^{33a} J. E. Leng, Ph.D. thesis, Purdue University, 1956.

Measurements of the thermal conductivity of nitrogen have been made by Michels and Botzen³⁴ to a pressure of 2,500 atm. The behavior of nitrogen in this pressure range is likely to be characteristic of low-molecular-weight spherically symmetrical molecules with nearly the same critical temperature. Figure 8-27 shows the variation of the thermal

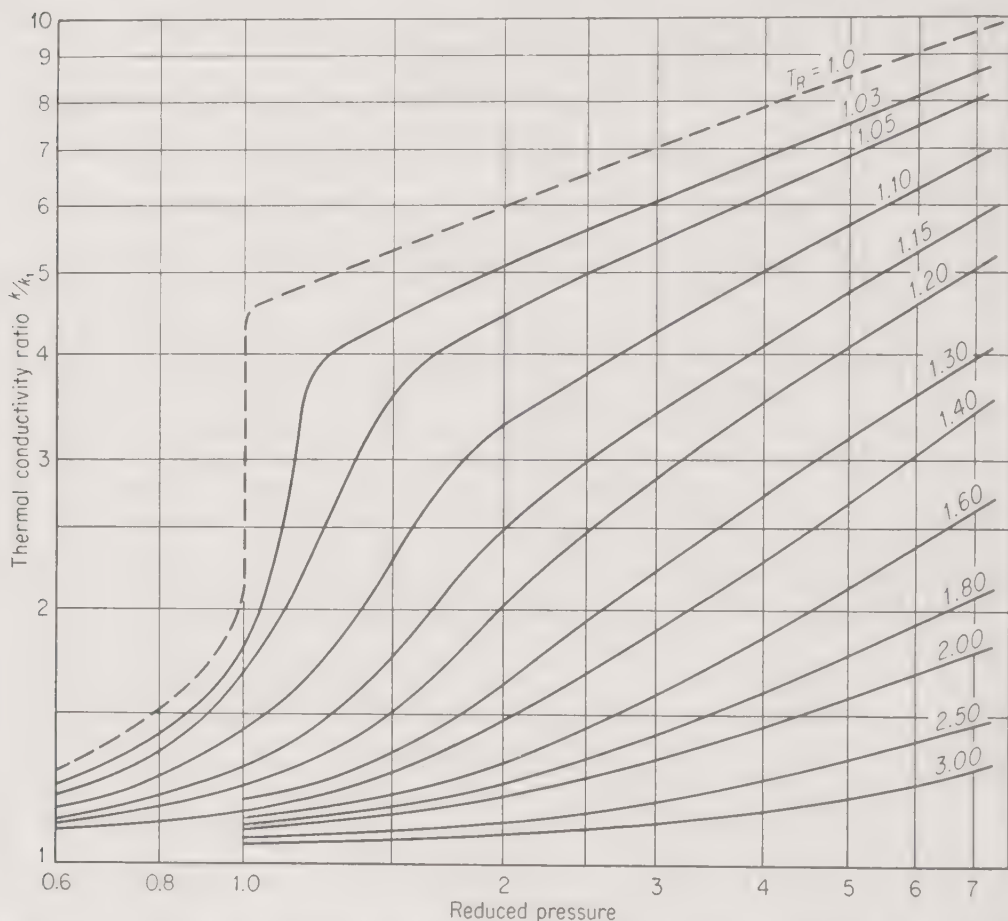


FIG. 8-26. Generalized correlation of thermal-conductivity ratio. [From J. M. Lenoir, W. A. Junk, and E. W. Comings, *Chem. Eng. Progr.*, **49**:539 (1953).]

conductivity with pressure at three temperatures. The same measurements are shown as a function of density in Fig. 8-28. The thermal conductivity rises steadily with density, the increase with density being more rapid at the higher densities. The relative effect of pressure on viscosity and thermal conductivity is shown in Fig. 8-29, where the ratio of the thermal conductivity to the viscosity is plotted as a function of pressure. This ratio is relatively constant but increases somewhat with pressure and then decreases at higher pressures.

³⁴ A. Michels and A. Botzen, *Physica*, **19**:585 (1953).

The behavior of the thermal conductivity of mixtures at elevated pressure does not follow an easily explained pattern. The thermal conductivity of mixtures of nitrogen and ethylene³⁵ is shown in Fig. 8-30, and that of carbon dioxide and ethylene in Fig. 8-31. An attempt was made to predict the values for the mixtures by using the pseudocritical temperature and pseudocritical pressure as defined by Kay [see Eqs. (8-110) and (8-111)]. This method predicted the measured values for the nitrogen-ethylene system with an average deviation of about 5 per cent.

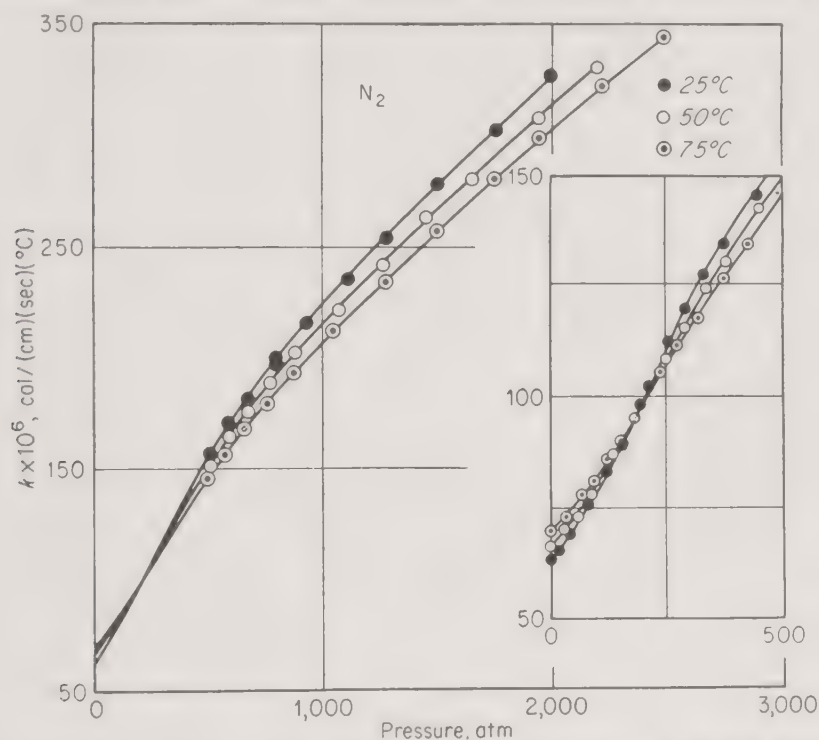


FIG. 8-27. Thermal conductivity of nitrogen vs. pressure to 3,000 atm. [From A. Michels and A. Botzen, *Physica*, **19**:585 (1953).]

The values predicted for the carbon dioxide-ethylene mixture were in error by as much as 50 per cent. It is evident that Kay's method cannot be applied to the thermal conductivity of gas mixtures. At pressures from 85 to 200 atm, the thermal conductivity of a mixture of 55.5 mole per cent ethylene and 44.5 mole per cent carbon dioxide was lower than that of either ethylene or carbon dioxide as pure gases at the same temperature and pressure. Thus no conventional method of calculating an average value for the mixture from the values of the pure components can be applied.

Prediction of the Prandtl Number. In the design of heat-transfer equipment, it is frequently necessary to predict the effect of pressure on the

³⁵ W. A. Junk and E. W. Comings, *Chem. Eng. Progr.*, **49**:263 (1953).

Prandtl number $c_p\mu/k$. This effect can be expressed by the ratio $\frac{c_p\mu/k}{c_{p1}\mu_1/k_1}$. It has been shown in Figs. 8-24 and 8-26 that both μ/μ_1 and k/k_1 are functions of the reduced temperature and reduced pressure.

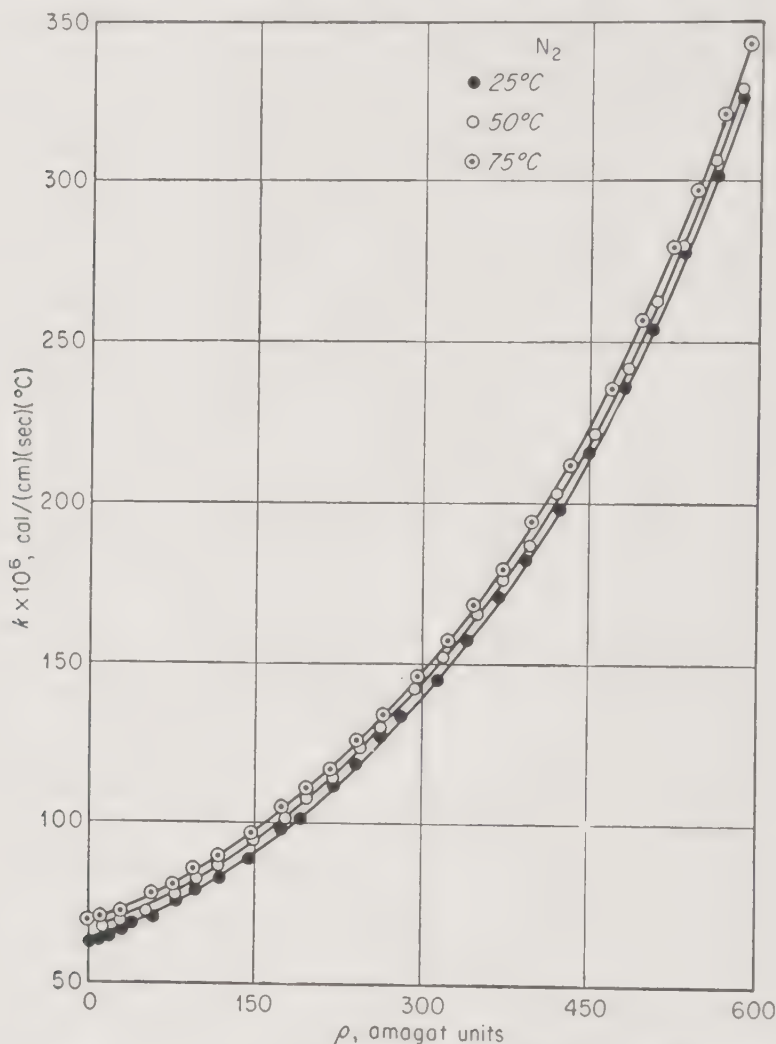


FIG. 8-28. Thermal conductivity of nitrogen vs. density. [From A. Michels and A. Botzen, *Physica*, **19**:585 (1953).]

These functions may be expressed as

$$\frac{\mu}{\mu_1} = f_1(p_R, T_R) \quad (8-91)$$

and

$$\frac{k}{k_1} = f_2(p_R, T_R) \quad (8-92)$$

Comings and Nathan³² have shown that only the difference $M(c_p - c_{p1})$ and not the ratio c_p/c_{p1} is a function of the reduced temperature and

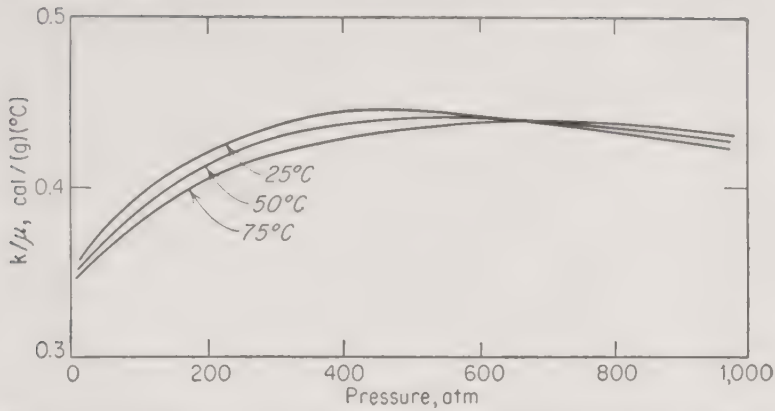


FIG. 8-29. Ratio of thermal conductivity to viscosity of nitrogen vs. pressure. [From A. Michels and A. Botzen, *Physica*, **19**:585 (1953).]

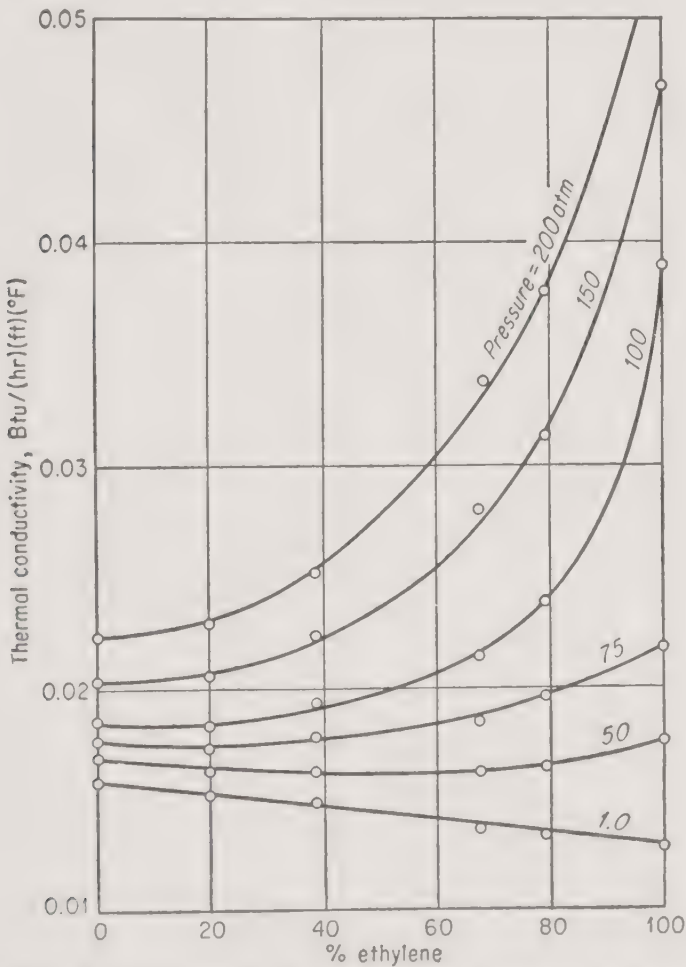


FIG. 8-30. Thermal conductivity of mixtures of nitrogen and ethylene. [From W. A. Junk and E. W. Comings, *Chem. Eng. Progr.*, **49**:263 (1953).]

the reduced pressure. Thus

$$Mc_p - Mc_{p1} = f_3(p_R, T_R) \quad (8-93)$$

It follows that

$$\frac{c_p \mu / k}{c_{p1} \mu_1 / k_1} = \frac{f_1 / f_2}{(f_3 / Mc_{p1}) - 1} = f_4(p_R, T_R, Mc_{p1}) \quad (8-94)$$

In other words, the Prandtl-number ratio as given on the left side of Eq. (8-94) is a function of Mc_{p1} as well as of the reduced pressure and

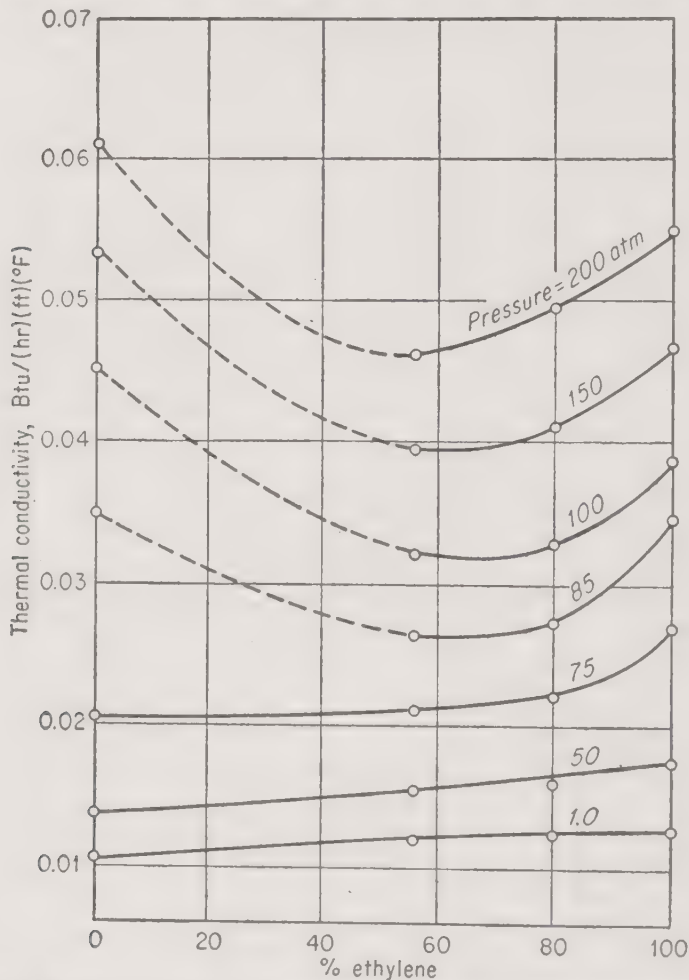


FIG. 8-31. Thermal conductivity of mixtures of carbon dioxide and ethylene. [From W. A. Junk and E. W. Comings, *Chem. Eng. Progr.*, **49**:263 (1953).]

the reduced temperature. This ratio can be calculated by first obtaining μ/μ_1 from Fig. 8-24, k/k_1 from Fig. 8-26, and $Mc_p - Mc_{p1}$ from Fig. 8-20, and then combining these as indicated by Eq. (8-94).

Thermal Conductivity of Liquids. The thermal conductivity of 53 pure organic liquids was measured by B. C. Sakiadis and J. Coates.³⁶ These

³⁶ B. C. Sakiadis and J. Coates, *AIChE J.*, **1**:275 (1955).

authors also presented semiempirical procedures for predicting the thermal conductivity of liquids. The procedures are based on an equation originally developed by Kardos which they rederived and interpreted in a more careful manner. This equation is

$$k = c_p U_s \rho L \quad (8-95)$$

Reference should be made to the original paper for methods for calculating U_s and L . When using these methods for calculating the values of the thermal conductivity, the average deviation from the observed values for 42 liquids was ± 2.6 per cent. The maximum deviation was ± 6 per cent.

Equation (8-95) should be applicable to predicting the effect of pressure on the thermal conductivity of liquids. The authors did not describe the procedure for doing this, and the data available for comparison with such calculations are meager. Bridgman³⁷ found that the change in the thermal conductivity of liquids with pressure was small.

8-11. Molecular Diffusion in Gases. The transport of matter takes place by molecular diffusion when there is a concentration gradient in a mixture which is otherwise in a uniform, quiescent condition. Under these conditions for a mixture of two components at uniform temperature, the rate of mass transfer by diffusion is

$$N_1 = -D_{12} \frac{\partial c_1}{\partial x} \quad (8-96)$$

The mutual-diffusion coefficient D_{12} for gases at low pressures is given to a close approximation³⁸ by an equation of the form

$$D_{12} = \frac{f_{12}(T)}{c_m r_0^2} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} = \frac{RT}{pr_0^2} f_{12}(T) \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \quad (8-97)$$

where M_1 and M_2 are the molecular weights of components 1 and 2, respectively. Until recently little has been known about the diffusion of gases at elevated pressures. Techniques employing radioactive isotopes to distinguish between isotopes of the same element have now been used to reveal the effect of pressure on self-diffusion. This is the diffusion of molecules through other molecules of the same element or compound. Enskog's³ dense-gas theory is based on the concept of molecules being hard spheres and is the only available theoretical treatment at the present time. Equation (8-97) indicates that $D_{12}c$ should be constant for a given mixture at constant temperature. O'Hern and Martin³⁸ have found this product constant for diffusion in the system $C^{12}O_2$ - $C^{14}O_2$ between 0 and $100^\circ C$ and up to 400 times the density at 1 atm. Robb and

³⁷ P. W. Bridgman, *Am. Acad. Arts Sci.*, **49**:141 (1923).

³⁸ H. A. O'Hern, Jr., and J. J. Martin, *Ind. Eng. Chem.*, **47**:2081 (1955).

Drickamer³⁹ agree with this conclusion at densities up to 200 times the density at atmospheric pressure. Timmerhaus and Drickamer⁴⁰ extended the measurements on this system to 1,000 atm and found a marked decrease in the D_{12c} product with increase in pressure. Such a decrease is predicted by the Enskog dense-gas theory. Timmerhaus and

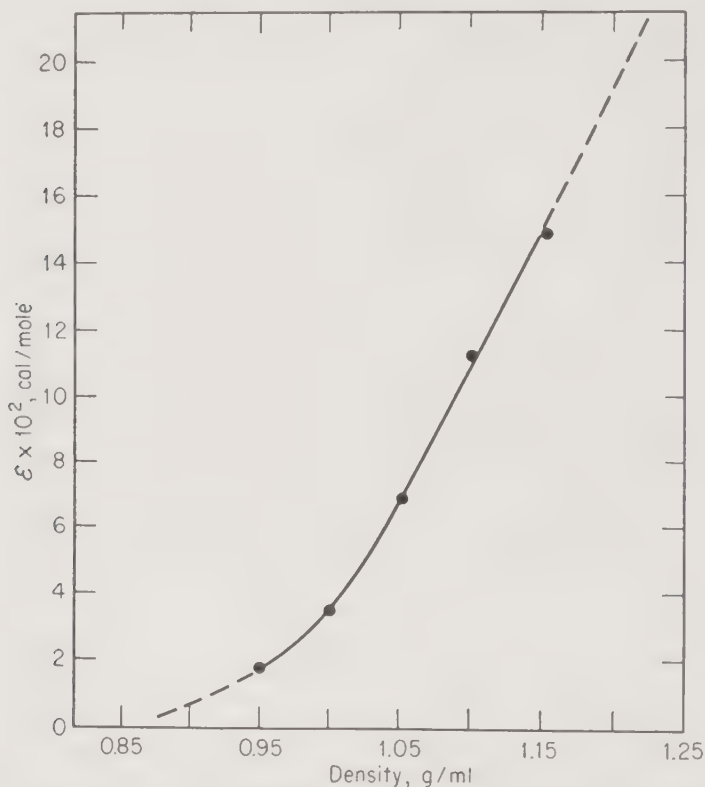


FIG. 8-32. Activation energy for diffusion of carbon dioxide vs. density. [From K. D. Timmerhaus and H. G. Drickamer, *J. Chem. Phys.*, **20**:981 (1952).]

Drickamer found that the diffusivity of carbon dioxide was well correlated by the equation

$$D = D_0 e^{-\epsilon/RT} \quad \text{at constant density} \quad (8-98)$$

where ϵ is the activation energy for diffusion. The values of ϵ and D_0 are both functions of the density, as shown by Figs. 8-32 and 8-33.

The self-diffusion of methane was determined by Jeffries and Drickamer⁴¹ at pressures up to 300 atm. The variation in D followed closely an equation obtained by combining the Enskog equation for dense gases with the collision-cross section integral for the Lennard-Jones model cal-

³⁹ W. L. Robb and H. G. Drickamer, *J. Chem. Phys.*, **19**:1504 (1951).

⁴⁰ K. D. Timmerhaus and H. G. Drickamer, *J. Chem. Phys.*, **20**:981 (1952).

⁴¹ Q. R. Jeffries and H. G. Drickamer, *J. Chem. Phys.*, **21**:1358 (1953).

culated by Hirschfelder, Bird, and Spotz.⁴² This equation is

$$D = \frac{3/16 (kT/\pi v)^{1/2}}{r_0^2 \varphi'' c \mathfrak{X}} \quad (8-99)$$

where $\mathfrak{X} = 1 + \frac{5}{12} \pi c \sigma^3 + 0.1275 (\pi c \sigma^3)^2 + \dots$

Diffusion in the system carbon dioxide-methane was observed by Jeffries and Drickamer⁴³ to 225 atm, and the diffusivity was reasonably

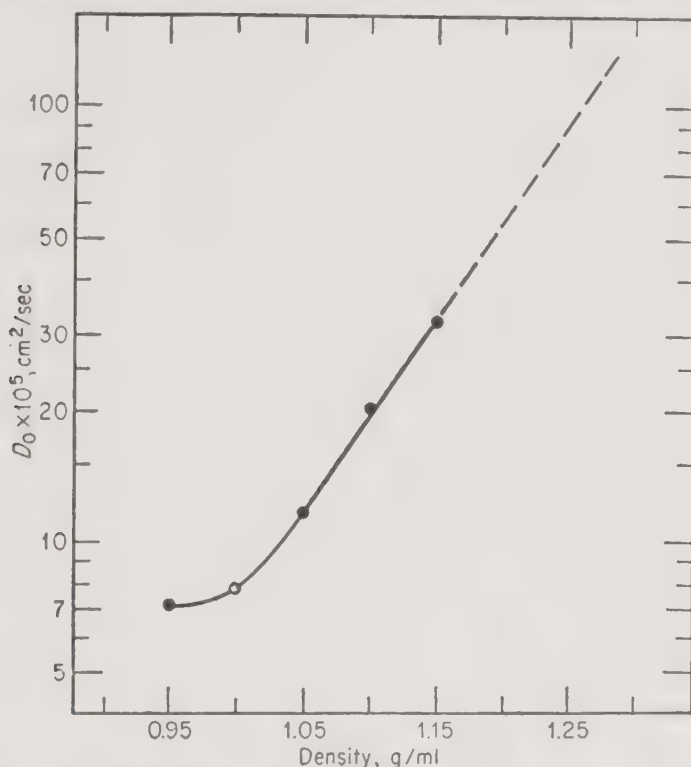


FIG. 8-33. Value of D_0 for diffusion of carbon dioxide vs. density. [From K. D. Timmerhaus and H. G. Drickamer, *J. Chem. Phys.*, **20**:981 (1952).]

described by Eq. (8-99). The measurements of diffusivity in the system just discussed are shown in Fig. 8-34 as the product $D\rho$ vs. the density of the mixture. Consistent agreement is not yet available as to the effect of pressure on the diffusivity in gases at elevated pressures.

Molecular Diffusion in Liquids. The effect of pressures as high as 10,000 atm on molecular diffusion in liquids has been measured in mixtures of carbon disulfide with a number of organic compounds, in water, and in sulfate solutions by Cuddeback, Koeller, and Drickamer.⁴⁴ The

⁴² J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *Chem. Revs.*, **44**:205 (1949); *J. Chem. Phys.*, **16**:968 (1948); *Trans. ASME*, **71**:921 (1949); also C. F. Curtis and J. O. Hirschfelder, *J. Chem. Phys.*, **17**:550 (1949).

⁴³ Q. R. Jeffries and H. G. Drickamer, *J. Chem. Phys.*, **22**:436 (1954).

⁴⁴ R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.*, **21**:575 (1953); R. B. Cuddeback, R. C. Koeller, and H. G. Drickamer, *J. Chem. Phys.*, **21**:589 (1953).

relatively small changes in the density of the liquid over this pressure range are accompanied by major changes in the diffusivity, and these do not follow the general predictions of available theoretical or empirical equations. These authors visualize diffusion as occurring by the movement of one species of molecule through the nonrigid lattice or matrix of other molecules. The matrix may be composed of molecules which do not move so rapidly as the diffusing molecules. This slower motion would be due to their greater size or complexity or to intermolecular forces which bind them together in loosely defined groups or aggregations such as those which persist when a crystal melts. While the liquid

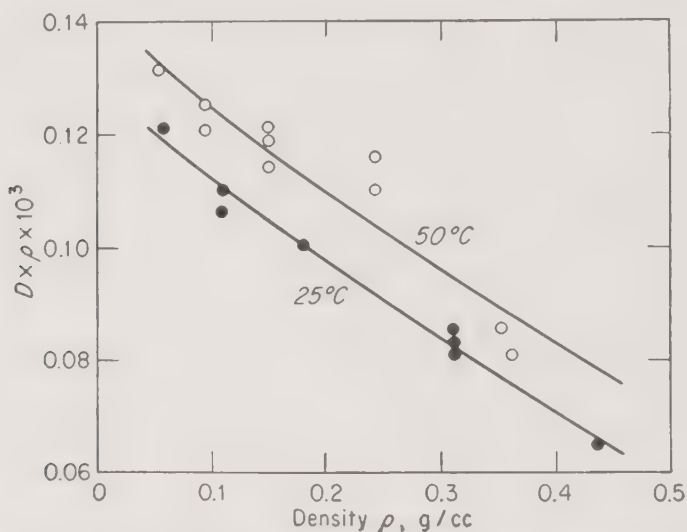


FIG. 8-34. The product $D\rho$ vs. ρ at pressures up to 225 atm for 50 mole per cent carbon dioxide-50 mole per cent methane. [From Q. R. Jeffries and H. G. Drickamer, *J. Chem. Phys.*, **22**:436 (1954).]

molecular lattice is not a stable arrangement comparable to a solid crystal lattice, nevertheless it may have residence times that are long compared to those of the diffusing molecules. Pressure has a pronounced effect on the liquid lattice, and this is reflected in large changes in the diffusivity of the diffusing molecules. The combination of variations in temperature and pressure is at times accompanied by anomalous variations in diffusivity. Examples of this behavior are shown in Fig. 8-35, which represents the self-diffusion of water in water, and in Fig. 8-36, which represents the diffusion of 0.1 normal sodium sulfate. The 0°C curve for water is strongly influenced by the residual clustering of molecules in the lattice for ice, while the curves at 25 and 50°C display distinctly different behavior with pressure. The maximum and minimum at the low-pressure end of the 0°C curve for sodium sulfate are also reminiscent of the behavior of water at this temperature.

Thermal Diffusion. Heat may be transferred through a stagnant fluid as a result of a concentration gradient instead of a temperature gradient. Also, matter may be transferred as the result of a temperature gradient

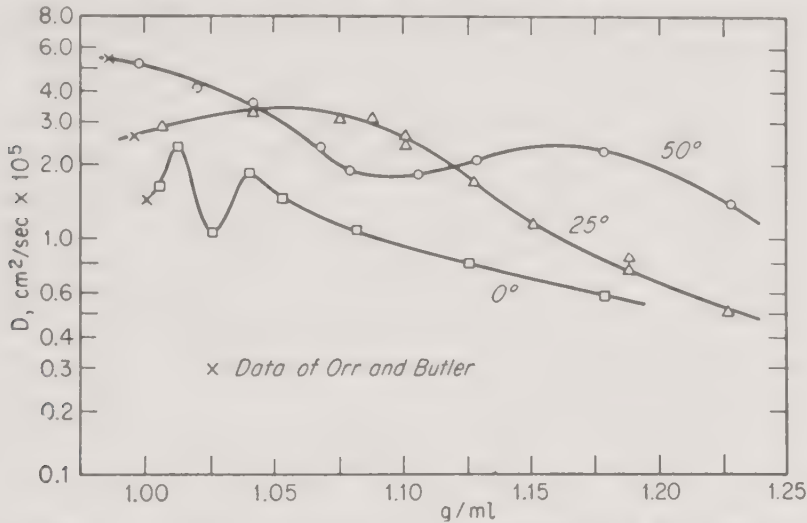


FIG. 8-35. Diffusion coefficients for the system THO-H₂O as a function of density. [From R. B. Cuddeback, R. C. Koeller, and H. G. Drickamer, *J. Chem. Phys.*, **21**:589 (1953).]

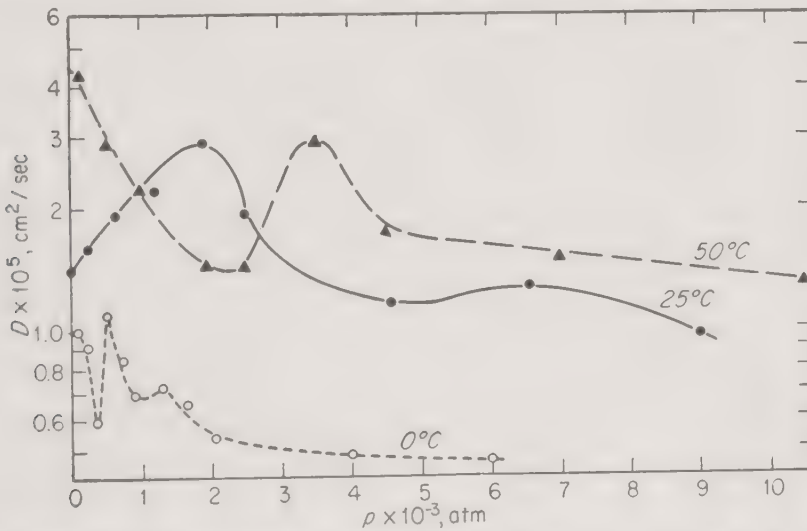


FIG. 8-36. Diffusion coefficients vs. pressure for 0.1 N Na₂SO₄. [From R. B. Cuddeback, R. C. Koeller, and H. G. Drickamer, *J. Chem. Phys.*, **21**:589 (1953).]

rather than a concentration gradient. The latter is called thermal diffusion, and α is the thermal-diffusion ratio. When the transfer of matter occurs where there are both a concentration gradient and a temperature gradient, the rate of mass transfer by diffusion is given by

$$N_1 = -D_{12} \left(\frac{\partial c_1}{\partial x} - \alpha c_1 c_2 \frac{\partial \ln T}{\partial x} \right) \quad (8-100)$$

Caskey and Drickamer⁴⁵ have measured values of α for isotopic mixtures of C^{12}O_2 and C^{14}O_2 and for CH_4 and CH_3H^3 at pressures extending above the critical region. For small molecules with some degree of spherical symmetry such as carbon dioxide and methane, these authors suggest that the measured values of α/α_0 follow a general pattern based

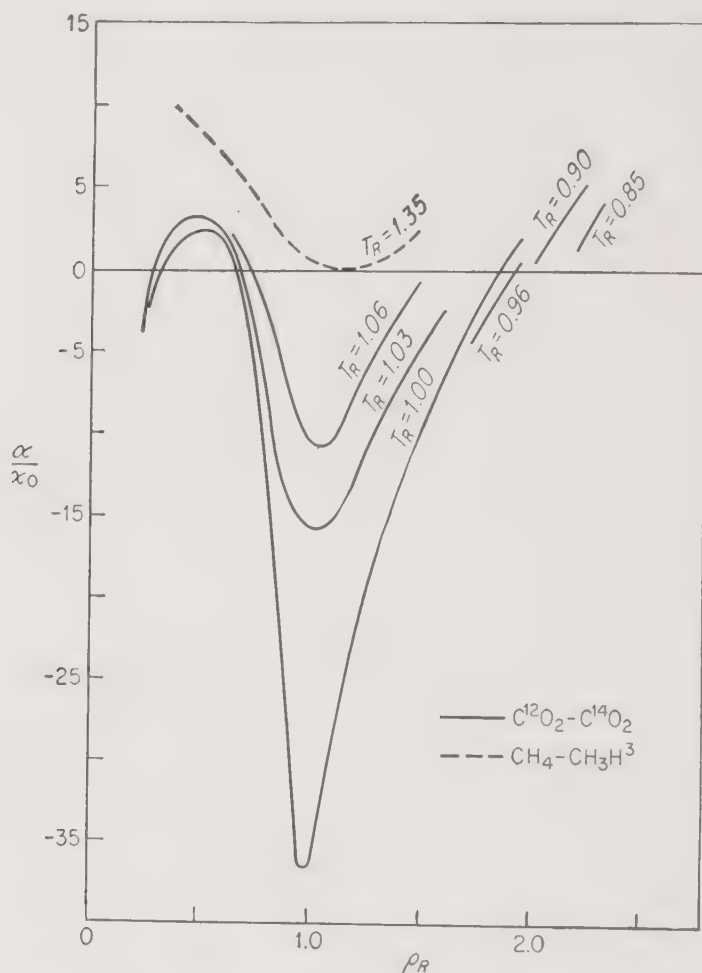


FIG. 8-37. Thermal-diffusion ratio vs. reduced density at constant reduced temperature. [From F. E. Caskey and H. G. Drickamer, *J. Chem. Phys.*, **21**:153 (1953).]

on the theorem of corresponding states. Their correlation of α/α_0 vs. the reduced density at constant values of reduced temperature is shown in Fig. 8-37. This ratio for carbon dioxide assumes large negative values in the vicinity of the critical point. At lower and higher densities, the values are smaller and are both positive and negative.

8-12. Mixture of Substances. The information presented in the preceding text applies largely to pure substances and is useful when gases or

⁴⁵ F. E. Caskey and H. G. Drickamer *J. Chem. Phys.*, **21**:153 (1953).

vapors are to be stored or handled as relatively pure materials. Frequently they will be found in nature or prepared and used in industrial processes as mixtures of two or more compounds. The experimental determination of the physical and thermal properties and of the phase behavior of all mixtures of industrial importance is perhaps impossible, and the prediction of these with some degree of accuracy is therefore

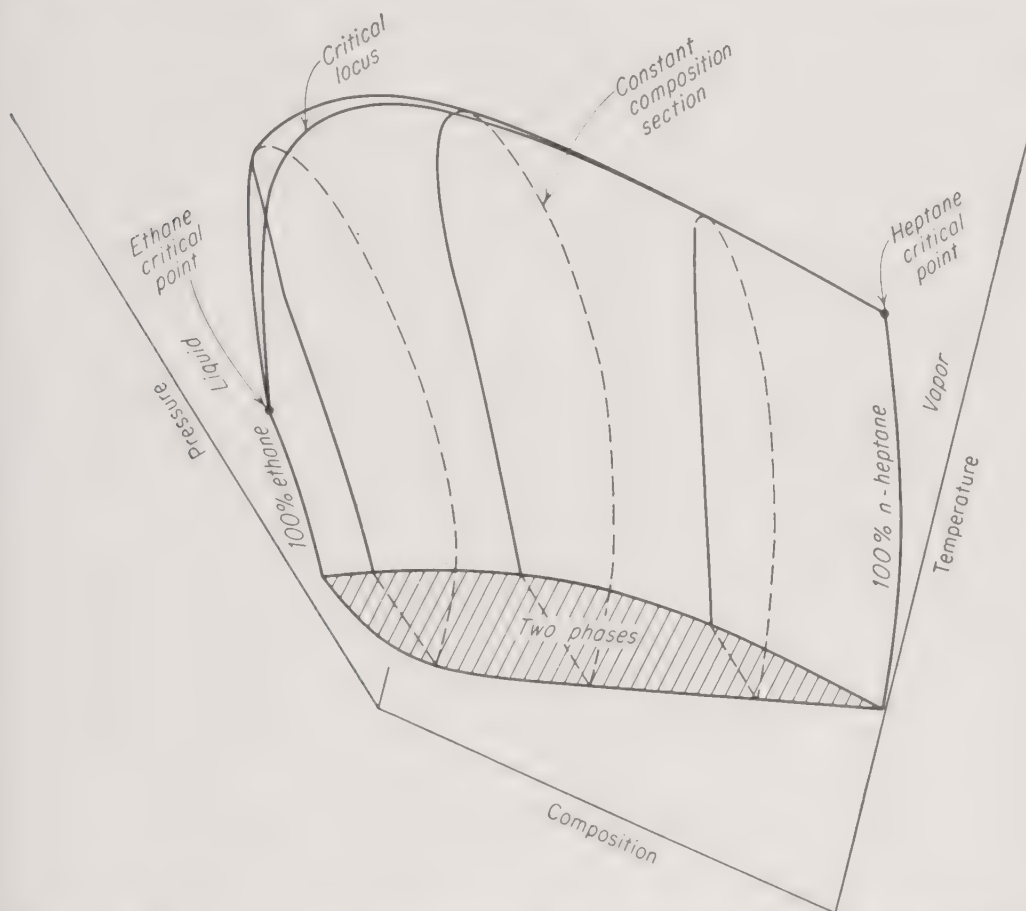


FIG. 8-38. Model representing the relation among temperature, pressure, and composition for the system ethane and *n*-heptane. [Data from W. B. Kay, *Ind. Eng. Chem.*, **30**:459 (1938).]

necessary. Considerable progress has been made in recent years in developing methods for making these predictions. Nevertheless, the properties of mixtures, especially at high pressures, can as yet be predicted only approximately in many instances.

Phase Behavior. A system composed of two compounds which behaves normally will serve to illustrate the marked difference between the phase behavior of a simple multicomponent system and that of a system containing a single component. Figure 8-38 represents a typical two-com-

ponent system in the three coordinates⁴⁶ pressure, temperature, and mole fraction x . The two lines at the sides of the diagram where $x = 0$ and $x = 1$ are the vapor-pressure curves for the two pure components in the mixture. Only for pure components is there a single value of the vapor pressure at a given temperature where a vapor and a liquid of the same composition are in equilibrium. The upper and lower surfaces of the solid figure between $x = 0$ and $x = 1$ represent the phase boundaries between the vapor phase, below, and the liquid phase, above. At all points within the solid figure, a mixture of two phases exists, each phase having a composition on the upper and lower surfaces, respectively. The average composition of the mixture of two phases is given by a point between the two surfaces. Constant-composition slices are shown through the solid to indicate its shape. The points at maximum temperature and pressure on the two vapor-pressure curves for the pure components are the critical points for these two pure compounds. The upper boundary of the two-component region does not have a sharp edge but is rounded, and this raises a question as to the significance of the critical point of a mixture. As in the case of a pure compound, the vapor of the mixture may be completely changed to a liquid without a definite phase change if a path is chosen that passes around the solid figure through temperatures and pressures above those in the critical region. If, on the other hand, the path representing pressures and temperatures passes through the solid figure, a definite interface is formed between the two phases and the phase change can be observed. The change from vapor to liquid, or vice versa, does not take place at a definite temperature and pressure as it does with a pure compound. When the path touches the lower surface of the figure, liquid begins to form, and this surface is thus the dew-point surface. As conditions are changed progressively and the path penetrates the figure, liquid continues to condense, and the condensation is complete at the upper surface. In the reverse process of vaporizing a liquid, a similar situation exists and vapor begins to form when the path meets the upper surface. This is called the bubble-point surface. The vaporization may be effected by increasing the temperature at constant pressure, decreasing the pressure at constant temperature, or any combination of changes in pressure and temperature which penetrates the solid figure. When a vapor condenses, the composition of the liquid phase is usually different from that of the vapor phase until condensation is complete, and then the final liquid has the same composition as the initial vapor. A similar situation exists when a liquid evaporates.

Consider a mixture with a given composition subjected to a temper-

⁴⁶ H. W. B. Roozeboom, "Die heterogenen Gleichgewichte von Standpunkte der Phasenlehre," Heft 2, Vieweg-Verlag, Brunswick, Germany, 1904.

ature and pressure such that its condition will be represented by a point within the solid figure. The mixture is then partially vapor and partially liquid. Since these phases are in equilibrium, they are at the same temperature and pressure but differ in composition. The composition of these two phases is determined by a line at constant temperature and

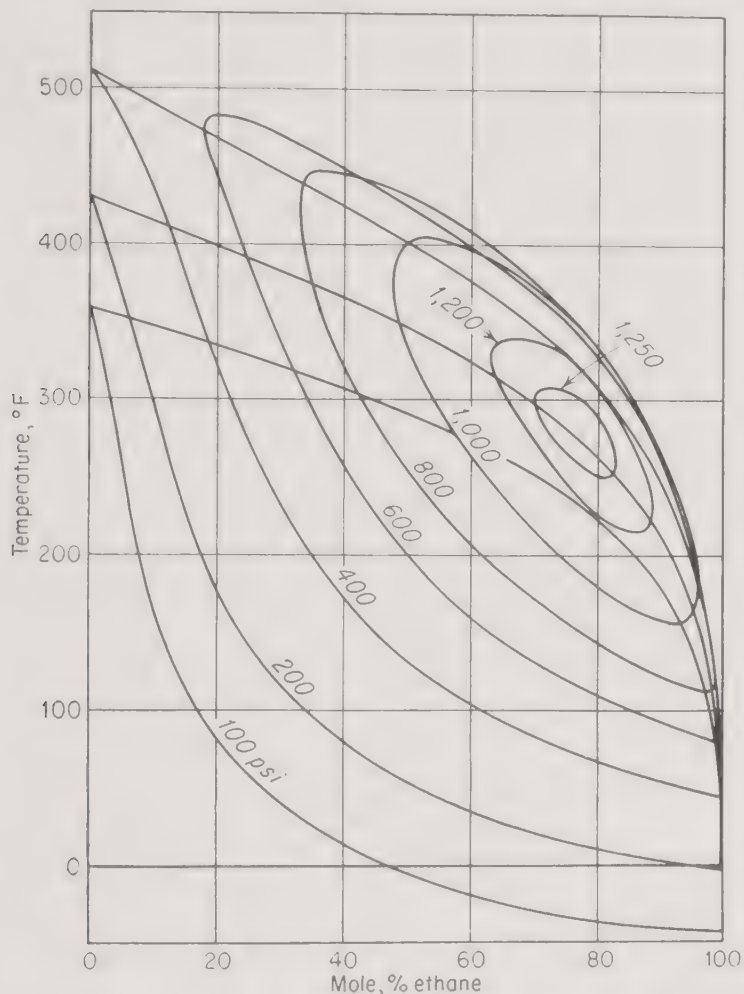


FIG. 8-39. Temperature-composition diagrams at constant pressure for mixtures of ethane and *n*-heptane. [From W. B. Kay, *Ind. Eng. Chem.*, **30**:463 (1938).]

pressure which intersects the dew-point surface and the bubble-point surface at the respective compositions of these phases. The relative masses of the two phases must also satisfy a material balance for the initial mixture and the final two-phase condition. In Figs. 8-39 to 8-41, sections are shown through the figure at constant pressure, constant temperature, and constant composition, respectively.⁴⁷ A single section at a constant composition cannot show the composition of two phases in

⁴⁷ W. B. Kay, *Ind. Eng. Chem.*, **30**:459 (1938).

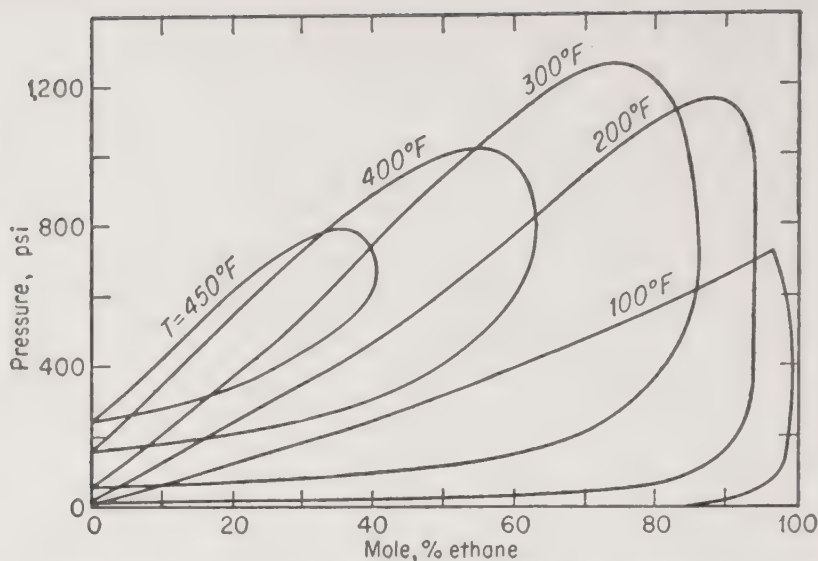


FIG. 8-40. Pressure-composition diagrams at constant temperature for mixtures of ethane and *n*-heptane. [Data from W. B. Kay, *Ind. Eng. Chem.*, **30**:459 (1938).]

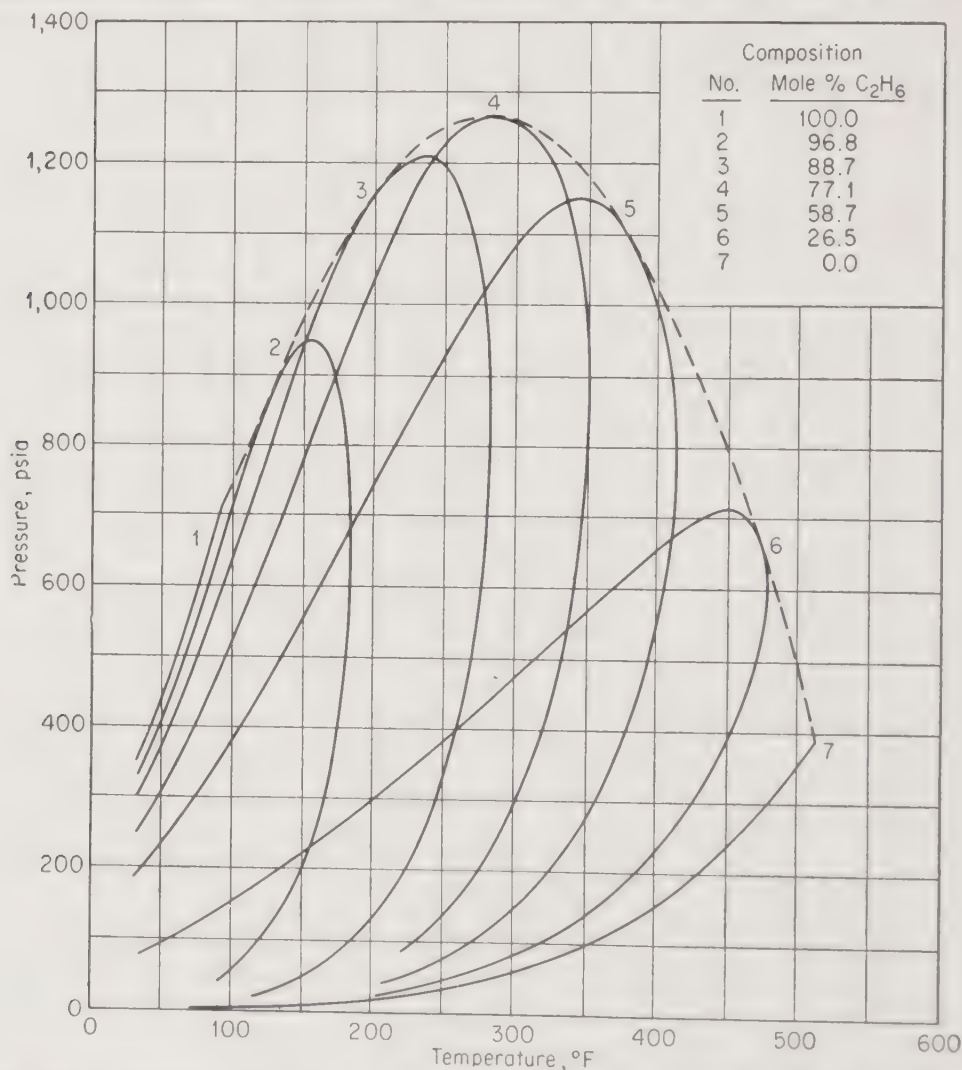


FIG. 8-41. Pressure-temperature diagrams at constant composition for mixture of ethane and *n*-heptane. [From W. B. Kay, *Ind. Eng. Chem.*, **30**:461 (1938).]

equilibrium since these phases will always have different compositions. Either the section at constant pressure or that at constant temperature may be used for this purpose.

Attention is directed to the behavior in the region of the critical. This is illustrated in Fig. 8-42 by a section at constant composition. This curve is called the border curve for the mixture. The critical temperature and critical pressure for the mixture are defined as the temperature and pressure at which the liquid and vapor phases of this composition

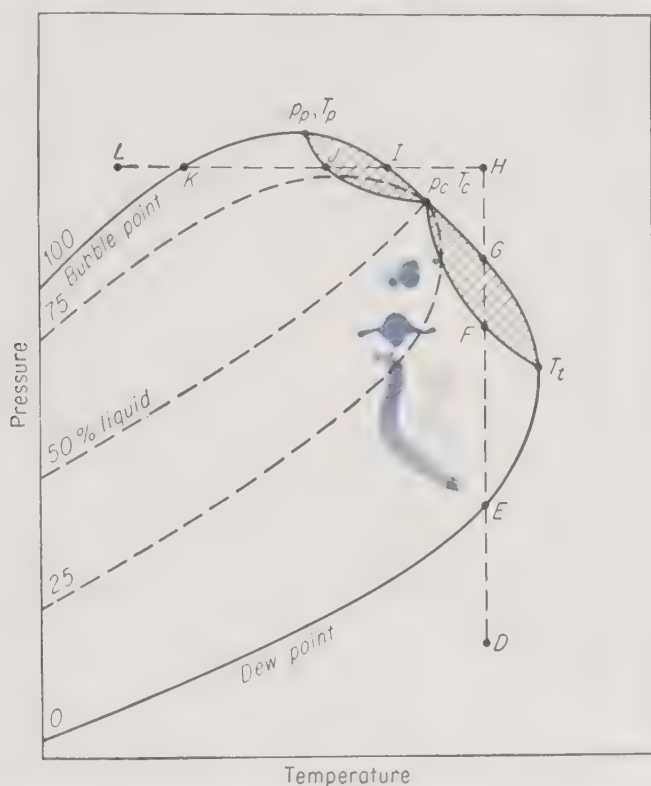


FIG. 8-42. Typical border curve at constant composition for a mixture of two components. [From D. L. Katz and F. Kurata, *Ind. Eng. Chem.*, **32**:817 (1940).]

have the same density. The location of this critical point is not evident from the shape of the border curve and must be located experimentally. It does not necessarily coincide with the maximum temperature T_t of the border curve nor with the maximum pressure p_p , but it usually lies on the border curve between these at some point represented by p_c and T_c in Fig. 8-42. The relative amounts of liquid and vapor in the two-phase region are shown by the lines of constant-percentage liquid which radiate from the critical point and follow somewhat parallel to the single-phase boundaries or border curves. The maximum temperature T_t on the dew-point curve of a given composition is termed the cricondentherm. This is the maximum temperature at which two phases can be formed from

this composition. The phases formed at this temperature will in general have unequal densities, and this point does not conform to the conditions defined for the critical point of the mixture. The pressure at the cricondentherm may differ widely from the maximum pressure for the existence of two phases. This maximum pressure at which two phases can be formed from this composition lies on the bubble-point curve at p_p .

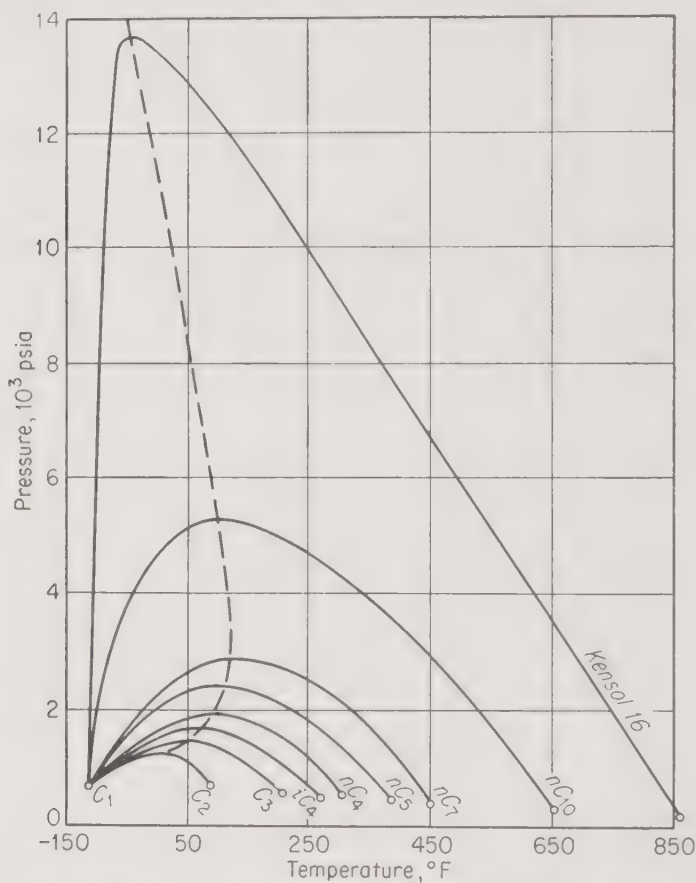


FIG. 8-43. Critical pressure of mixtures of hydrocarbons. [From M. J. Rzasa and D. L. Katz, *Trans. Am. Inst. Mining Met. Engrs.*, **189**:119 (1950).]

It is evident from Fig. 8-38 that both the critical pressure and the maximum pressure for a mixture of a given composition are frequently higher than the critical pressures of any of the pure components of the mixture. In Fig. 8-43 is shown the envelope curves for the critical points of several binary⁴⁸ hydrocarbon systems. These curves end at the critical pressures of the pure components. When the critical temperatures of the two components in a mixture differ widely, the critical pressure of certain compositions of the mixture may be several times the critical pressure of either of the pure components.

⁴⁸ M. J. Rzasa and D. L. Katz, *Trans. Am. Inst. Mining Met. Engrs.*, **189**:119 (1950).

Retrograde Behavior. The region adjacent to the critical point for a mixture and extending to the maximum pressure p_p and the criconden-therm T_c , as indicated by the shaded area in Fig. 8-42, is unusual in certain respects.⁴⁹ It will be recalled that the condensation of a vapor normally requires either a decrease in its temperature or an increase in its pressure, and vice versa for the evaporation of a liquid. This is always true of a pure substance and is true for a mixture except in regions such as this shaded area. The behavior in the shaded area is unusual. Consider a single-phase fluid as at H . Let this be cooled by lowering its temperature to the point I while holding its pressure constant. The point I is on the bubble-point curve, and a second phase of lower density begins to form and vaporization continues as the temperature decreases through the shaded area to the point J . Reversing the procedure, an increase in temperature in this shaded region above the critical results in condensation. Since this behavior is the reverse of our usual experience, it is termed *retrograde vaporization* or *retrograde condensation*. If as another alternative the pressure on the fluid at H is reduced at constant temperature to the point G on the dew-point curve, a more dense phase begins to form and retrograde condensation proceeds as the pressure decreases to the point F . Further reduction in pressure results in vaporization until at E the mixture is again a single, saturated vapor phase. In the first case, decreasing the temperature of a single phase has produced first a less dense phase. On further cooling, this phase is converted to liquid. In the second case, a decrease in pressure first produces a more dense phase. With further reduction in pressure, this phase is converted to vapor. The retrograde region is very extensive in multicomponent systems with a broad range of component critical temperatures.

The retrograde behavior is associated with curvature of the bubble-point curve such that an isobar will intersect it at two points, or it is associated with curvature of the dew-point curve such that an isotherm will intersect it at two points. Such curvature is found in some systems in other regions than that adjacent to the critical point. A system may then have two separate retrograde regions⁵⁰ as shown in Fig. 8-44. The region in this figure which is not adjacent to the critical exhibits retrograde behavior only for isobaric changes and not for isothermal.

The normal behavior of the two-component system shown in Fig. 8-38 is also the simplest type of behavior that has been observed. This behavior occurs when both components are quite similar and are completely miscible in vapor and liquid phases. The phase behavior is then the normal vapor-liquid equilibria. With components of unlike charac-

⁴⁹ D. L. Katz and F. Kurata, *Ind. Eng. Chem.*, **32**:817 (1940).

⁵⁰ W. B. Kay, *Ind. Eng. Chem.*, **29**:501 (1941).

teristics, either the heavier or lighter phase may separate into two immiscible phases. At high pressures the designations liquid phase and gas phase lose their signification and should not be used for the more complex phase behavior. Lindroos and Dodge⁵¹ have measured the phase equilibria in the nitrogen-ammonia system at pressures from 1,000 to 3,800 atm. The critical temperatures of these two components are 126.5°K and 406.0°K, respectively. The great difference in critical temperatures would lead one to anticipate a more complex phase behavior than that shown in Fig. 8-38. In addition to vapor-liquid equilibrium

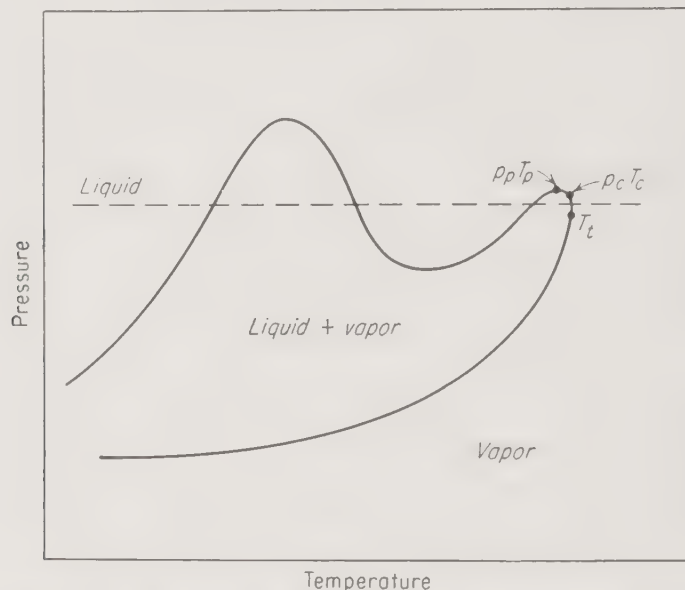


FIG. 8-44. Constant-composition-section for a mixture of two compounds with two retrograde regions. [From W. B. Kay, *Chem. Revs.*, **29**:501 (1941).]

observed at pressures below 1,000 atm, a barotropic phenomenon was observed as the pressure was increased above 1,800 to 2,000 atm. This type of behavior was originally predicted by van der Waals and has been observed more recently by Onnes⁵² and by Krichevsky and Bolshakov.⁵³ In barotropic phenomena, a phase which is initially the heavier phase becomes the lighter as pressure is increased. This behavior was observed in the nitrogen-ammonia system. The compressibility of nitrogen is apparently greater than that of ammonia at the temperatures and pressures involved. When the pressure is increased the density of the nitrogen-rich phase increases to a greater extent than that of the ammonia-rich phase and exceeds it as the pressure is increased above 1,800 to 2,100

⁵¹ A. E. Lindroos and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **48**(3):10 (1952).

⁵² H. K. Onnes, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **9**:459 (1906).

⁵³ I. R. Krichevsky and P. Bolshakov, *Acta Physicochim. U.R.S.S.*, **14**:353 (1941).

atm. There is no effect on the equilibrium other than a change in the relative position of the phases.

At pressures and temperatures above the critical point, a phase which was initially a gas phase at lower pressure may easily be compressed to a density considerably higher than the normal liquid density. Under these conditions the molecules are brought relatively close together, and the phase acts more nearly like a liquid phase, sometimes exhibiting limited miscibility. Thus, the types of behavior usually associated with liquid-liquid equilibrium may be observed in compressed-gas systems at high pressure. This behavior is illustrated by the nitrogen-ammonia system at a temperature slightly below the critical temperature of ammonia in Fig. 8-45. The region at low pressures for mixtures rich in ammonia displays the normal type of vapor-liquid equilibrium. Mixtures richer in nitrogen than x_1 appear to remain homogeneous at relatively high pressures. However, when the pressure is increased to several times that where the ordinary vapor-liquid equilibrium is observed, this homogeneous phase will separate into two phases as shown in the middle of Fig. 8-45. The upper part of the diagram has not been observed, but these effects may be expected to extend to pressures above 10,000 atm.

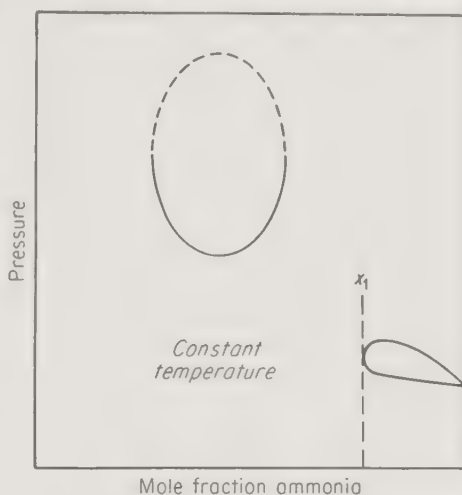


FIG. 8-45. Pressure-composition diagram for the system nitrogen-ammonia (not to scale). [From A. E. Lindroos and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **48**(3):10 (1952).]

8-13. Mixtures in a Single Phase. A mixture of several substances under low or moderate pressure may exist as a gas, liquid, or solid. Only gases and liquids will be discussed here. At elevated pressures, the density of a gas increases, and many of the distinctions between gases and liquids are then not so well defined. The tendency for a gas to become more like a liquid at high pressures should be kept in mind during the following discussion.

For a single-phase mixture the phase rule provides that the number of independent variables is equal to the number of components in the system plus 1. For a system of known mass composed of two components it will be necessary to choose combinations such as the pressure, the temperature, and the composition of the mixture, or the pressure, the composition, and the volume, to ensure that the system is in a defined or reproducible state. The behavior of a mixture in a single phase is most easily described

in precise terms when it is a gas at low pressures and obeys the perfect-gas law and is an ideal solution. As the pressure is increased, it ceases to behave as a perfect gas and at the same time ceases to behave as an ideal solution. Its behavior is then more complex. The complexity increases again when its density increases to that of the liquid. This may occur by condensation resulting either from a decrease in temperature or from an increase in pressure, or by compression alone without condensation. Gaseous mixtures will be discussed first, then liquid solutions, and finally the equilibrium between gases and liquids.

8-14. Gaseous Solutions. A gaseous mixture behaves as a perfect gas if it follows the perfect-gas law

$$pv = RT \quad (8-101)$$

and then the internal energy and the enthalpy depend on the temperature alone and are independent of pressure. The mixture behaves as an *ideal solution* if there is no difference between the sum of the volumes of its components alone and the volume of the mixture at any pressure up to the pressure of the solution.^{53a} Neither will there be any heat of mixing under these conditions in preparing an ideal solution from its components. Dalton's law and Amagat's law are applied to gaseous solutions. They lead to different results for real solutions. This will be clarified by defining these laws.

Additive Pressures. Consider a simple experiment in which two vessels with equal volume are filled, one with n_A moles of the gas A and the other with n_B moles of the gas B each at the same temperature. The pressures in the two vessels will be p_A and p_B . Now remove all the gas B from its vessel and add it to the vessel containing gas A at the same constant temperature. The pressure in the single vessel is then p , and, if the gases undergo mixing in such a way that they act independently of one another,

$$p = p_A + p_B \quad (8-102)$$

This is *Dalton's law* of additive pressures, and p_A and p_B are said to be the pure-component pressures of A and B, respectively, in the mixture.

If the pressure is high, the gas molecules of A will attract or repel those of B, and vice versa, and the pressure in the single vessel does not equal the sum of the pressures in the two vessels before mixing. In fact, the terms partial pressure of A and partial pressure of B in the mixture, commonly used at low pressures, then have no definite significance unless their meaning is arbitrarily defined. The partial pressure of A will be defined as

$$p'_A = y_A p \quad (8-103)$$

^{53a} H. C. Van Ness, *Chem. Eng. Sci.*, **4**:279 (1955).

This amounts to arbitrarily assigning to each component a partial pressure equal to a fraction of the total pressure proportional to the mole fraction of that component in the mixture. This partial pressure is not the pressure the pure component gas would exert if it alone were present in the vessel. That is,

$$p'_A + p'_B + \cdots = p \neq p_A + p_B + \cdots \quad (8-104)$$

A modification of Dalton's law proposed by Bartlett⁵⁴ suggests that $p''_A = y_A \bar{p}_A$, where \bar{p}_A is the pressure of A in a vessel when A alone is present at the same molar concentration as A and B combined. It is then predicted that $p = p''_A + p''_B$.

Dalton's law may be used to predict the volume of a mixture of known composition, pressure, and temperature. Pure-component pressures p_A and p_B , etc., are arbitrarily chosen for each component so that (a) their sum is the total pressure of the mixture, and (b) the volume of each component when alone under its pure-component pressure is the same for all components. This volume is the predicted volume of the mixture. This method requires a relation between the volume and pressure for the pure components. Any of the methods described in the preceding text for pure substances may be used to relate the pressure to the volume. These include actual experimental data, an equation of state such as van der Waals' or the Beattie-Bridgeman equation, or the general compressibility-factor correlation shown in Figs. 8-7 to 8-9. Using the latter, an average compressibility factor z_{av} may be defined as follows,

$$V = z_A n_A \frac{RT}{p_A} = z_B n_B \frac{RT}{p_B} = z_{av} \sum n \frac{RT}{p} \quad (8-105)$$

$$\text{Therefore} \quad z_A n_A \frac{RT}{\bar{V}} + z_B n_B \frac{RT}{\bar{V}} + \cdots = z_{av} \sum n \frac{RT}{\bar{V}}$$

$$\text{or} \quad z_{av} = \frac{z_A n_A + z_B n_B + \cdots}{\sum n} \quad (8-106)$$

where z_A and z_B are evaluated at p_A and T and at p_B and T , respectively.

Additive Volumes. Let n_A moles of A and n_B moles of B, both at the same temperature, be confined in the volumes V_A and V_B (pure-component volumes) which occupy opposite ends of a cylinder separated by an impermeable membrane of negligible thickness. Suppose now that both ends of the cylinder are closed by pistons which exert the same pressure p on both gases. Now remove the membrane and allow the gases to mix. For ideal mixing, the volume of the mixture is the same as the sum of the

⁵⁴ E. P. Bartlett, H. L. Cupples, and T. H. Tremearne, *J. ACS.*, **50**:1275 (1928).

pure-component volumes of A and B before the membrane was removed. Thus

$$V = V_A + V_B + \cdots \quad (8-107)$$

This is *Amagat's law*. For perfect gases Amagat's law follows directly from Dalton's law, and the two laws give identical results. For non perfect gases the two laws often differ very considerably. The prediction of the volume of a mixture of known composition, temperature, and total pressure is made by determining the volume of each component V_A and V_B as if it alone were present at the temperature and total pressure of the mixture (pure-component volumes). It follows that since $V_A + V_B + \cdots = V$,

$$z'_A n_A \frac{RT}{p} + z'_B n_B \frac{RT}{p} + \cdots = z'_{av} \sum n \frac{RT}{p} \quad (8-108)$$

Therefore
$$z'_{av} = \frac{z'_A n_A + z'_B n_B + \cdots}{\sum n} \quad (8-109)$$

where z'_A and z'_B are evaluated at the temperature and total pressure of the mixture. The values of z'_A and z'_B may be read from Figs. 8-7 to 8-9.

The definition of an ideal solution differs from the definition of a perfect gas. In general, a gaseous mixture behaves as an ideal solution only so long as it behaves as a perfect gas.² However, ideal-solution equations may give better results with real gases than do perfect-gas equations. The concepts of additive pressures and of additive volumes provide a basis for predicting the behavior of mixtures which is only partially satisfactory. The above discussion serves to illustrate the uncertainties encountered in using these concepts and the term partial pressure when the mixture does not behave as a perfect gas. Another method for predicting the volume of mixtures, which also is not entirely satisfactory but is frequently an improvement over these, will be described.

Pseudocritical Method. The variation of pressure with temperature at constant volume (an isometric) for a pure substance in the vapor region was shown to be nearly linear in Fig. 8-1. This linear variation of pressure with temperature along an isometric is also characteristic of mixtures in the vapor region. Figure 8-46 shows the vapor-pressure curve of a pure substance compared with the border curve of a mixture. The isometrics radiate from the vapor-pressure curve and from the border curve, and in general those of the mixture do not coincide with those of a pure substance. Kay⁵⁵ has shown that the isometrics of the vapor of a mixture may be satisfactorily predicted from the generalized compressibility factors given in Figs. 8-7 to 8-9 when a pseudocritical temperature and pseudocritical pressure for the mixture are properly chosen for evaluating

⁵⁵ W. B. Kay, *Ind. Eng. Chem.*, **28**:1014 (1936).

the reduced temperature and the reduced pressure. These are defined as the molal average of the critical temperatures of the components in the mixture and the molal average of their critical pressures.

$$p'_c = x_A p_{c_A} + x_B p_{c_B} + \dots \quad (8-110)$$

$$T'_c = x_A T_{c_A} + x_B T_{c_B} + \dots \quad (8-111)$$

where p'_c is the pseudocritical pressure for the mixture, and T'_c is the pseudocritical temperature for the mixture. It is evident from Fig. 8-46

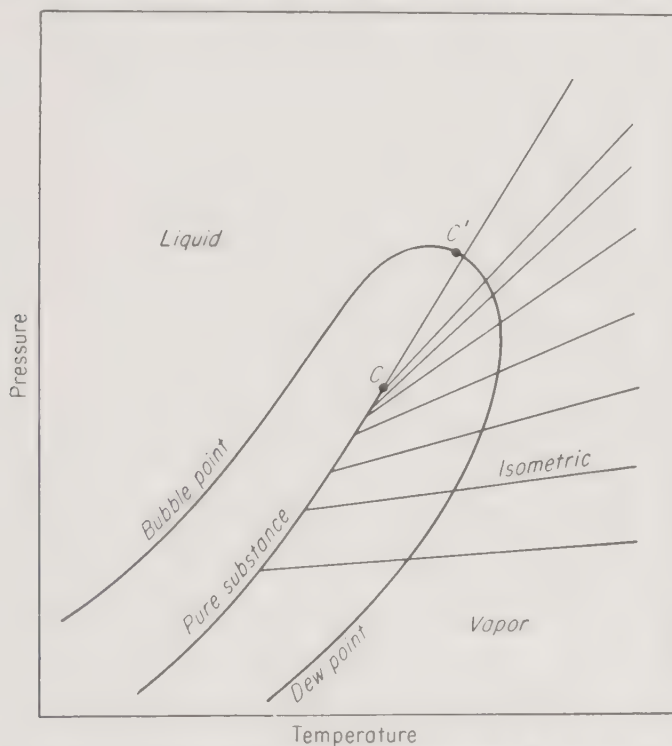


FIG. 8-46. Comparison of the vapor-pressure curve of a pure substance with the boundary curve of a mixture showing the isometrics. [From W. B. Kay, *Ind. Eng. Chem.*, **28**:1014 (1936).]

that the pseudocritical point C' for the mixture will, in general, lie well within the border curve and will not correspond to the true critical point C for the mixture. The pseudocritical point corresponds to the critical point of the equivalent pure substance with a molecular weight equal to the average molecular weight of the mixture. The isometrics of the equivalent pure substance will then coincide with those of the mixture in the single-phase vapor region. The linear isometrics do not have any significance for the mixture inside the border curve.

The procedure for applying the pseudocritical method consists of first determining the molal average critical temperature and the molal average critical pressure of the component mixture. This pseudocritical is then

used as though the mixture were a pure compound, and the compressibility factor for the mixture may be read from Figs. 8-7 to 8-9 at a reduced temperature taken as the ratio of the actual absolute temperature to the pseudocritical absolute temperature and at a reduced pressure equal to the ratio of the actual pressure to the pseudocritical pressure. The pseudocritical method gives no indication of the location of the border curve, and other methods are needed to indicate whether the predicted pVT relations are in the single-phase region.

The pseudocritical method proposed by Kay is suitable for moderate pressure up to perhaps 300 atm. Joffe^{56,57} has shown that another pair of equations gives better results at higher pressures than Eqs. (8-110) and (8-111) when used to define the pseudocritical temperature and pressure for mixtures. These equations are

$$\frac{T_c'''}{(p_c''')^{1/2}} = \sum_i \frac{x_i T_{c_i}}{p_{c_i}^{1/2}} \quad (8-112)$$

$$\frac{T_c'''}{p_c'''} = 1/8 \sum_i \sum_j x_i x_j \left(\frac{T_{c_i}^{1/3}}{p_{c_i}^{1/3}} + \frac{T_{c_j}^{1/3}}{p_{c_j}^{1/3}} \right)^3 \quad (8-113)$$

The modified critical constants for hydrogen, helium, and neon as proposed by Newton are used in place of the experimental values when these gases are included in a mixture.

Equation of State for Mixtures. A single-phase vapor mixture may be uniquely specified if the composition and two other properties or conditions such as pressure and temperature or temperature and molal volume are given. Extensive experimental data are required for the development of an equation of state relating the above two variables to a third, dependent variable for all possible compositions of a multicomponent mixture. As an example, such an equation could relate the variables p , v , T , x_1 , x_2 , etc. The labor involved in obtaining such an equation for mixtures is reduced by developing it from equations for the pure components. Equations of state for each pure component are put in a comparable form, and an equation of like form is obtained for mixtures of fixed composition. The equation for the mixture of constant composition may be obtained by evaluating its constants as the proper average of the constants of the equations for the pure components.

The Redlich and Kwong equation (8-17) is applied to a mixture of several components with the mole fractions y_1, y_2, \dots, y_j by using average values of the constants A and B for the mixture, determined from

⁵⁶ J. Joffe, *Ind. Eng. Chem.*, **40**:1738 (1948).

⁵⁷ J. Joffe, *Ind. Eng. Chem.*, **39**:837 (1947).

those for the pure components by the relations

$$A = \sum_j y_j A_j, \quad B = \sum_j y_j B_j \quad (8-114)$$

A_j and B_j are determined from Eqs. (8-21) and (8-22) for A and B for pure substances.

The eight constants in the Benedict-Webb-Rubin equation of state for a mixture may also be calculated from the constants for the pure components in the mixture. The constants for the mixture are evaluated from the following equations,

$$B_0 = \sum_j (y_j B_{0j}) \quad (8-115a)$$

$$A_0 = \left[\sum_j (y_j A_{0j}^{1/2}) \right]^2 \quad (8-115b)$$

$$C_0 = \left[\sum_j (y_j C_{0j}^{1/2}) \right]^2 \quad (8-115c)$$

$$b = \left[\sum_j (y_j b_j^{1/3}) \right]^3 \quad (8-115d)$$

$$a = \left[\sum_j (y_j a_j^{1/3}) \right]^3 \quad (8-115e)$$

$$c = \left[\sum_j (y_j c_j^{1/3}) \right]^3 \quad (8-115f)$$

$$\alpha = \left[\sum_j (y_j \alpha_j^{1/3}) \right]^3 \quad (8-115g)$$

$$\gamma = \left[\sum_j (y_j \gamma_j^{1/2}) \right]^2 \quad (8-115h)$$

The symbols with the subscript j , such as B_{0j} , b_j , etc., are the constants for the j th pure component in the mixture.

Methods for combining the constants of other equations of state are available in the literature.^{58,59,60}

8-15. Fugacities in Gas Mixtures. The fugacity concept will be found useful with mixtures, as it was for pure substances, in either the liquid or gas phase. The rigorous determination of the fugacity for each component of a mixture is possible when sufficient pVT -composition data are available for the system.¹⁷ The procedure is similar to that used for a

⁵⁸ J. D. van der Waals, "Die Continuität des gasförmigen und flüssigen Zustandes," Johann Ambrosius Barth Verlag, Leipzig, 1899.

⁵⁹ E. R. Gilliland, *Ind. Eng. Chem.*, **28**:212 (1936).

⁶⁰ J. A. Beattie, *J. ACS*, **51**:19 (1929).

pure compound except that the partial molal volume is substituted for the molal volume.

At constant temperature and composition

$$d\bar{F}_j = \bar{v}_j dp = RT d \ln \bar{f}_j \quad (8-116)$$

where \bar{F}_j = partial molal free energy of component j in the mixture

\bar{v}_j = partial molal volume of component j in the mixture

$$= \left(\frac{\partial v}{\partial n_j} \right)_{T, p, n_1, n_2, \dots}$$

\bar{f}_j = fugacity of j in the mixture

Let
$$\bar{z}_j = \frac{p\bar{v}_j}{RT} \quad (8-117)$$

which is the partial molal compressibility factor for j in the mixture, where \bar{z}_j is a function of temperature, pressure, and composition. From Eqs. (8-116) and (8-117)

$$d \ln \bar{f}_j = \bar{z}_j \frac{dp}{p} \quad (8-118)$$

$d \ln p$ may be added and subtracted to give

$$d \ln \bar{f}_j = d \ln p + \frac{\bar{z}_j - 1}{p} dp \quad (8-119)$$

At constant temperature and composition, Eq. (8-119) may be integrated from a low pressure p^* to the pressure of the mixture p at constant temperature and composition. Then

$$\ln \frac{\bar{f}_j}{\bar{f}_j^*} = \ln \frac{p}{p^*} + \int_{p^*}^p \frac{\bar{z}_j - 1}{p} dp \quad (8-120)$$

At sufficiently low pressure p^* , $p_j^* = y_j p^*$; then $\ln (p/p^*) = \ln (py_j/p_j^*)$, and

$$\ln \bar{f}_j = \ln y_j + \ln \frac{\bar{f}_j^*}{p_j^*} + \ln p + \int_{p^*}^p \frac{\bar{z}_j - 1}{p} dp \quad (8-121)$$

At low values of p^* , \bar{f}_j^*/p_j^* is unity and $\ln (\bar{f}_j^*/p_j^*)$ is zero. The fugacity of the component j in the mixture may be calculated from Eq. (8-121) by using pVT composition data to evaluate the integral on the right.

It will be recalled that Eq. (8-60) gives the fugacity for the pure substance j as

$$\ln f_j = \ln p + \int_0^p \frac{z_j - 1}{p} dp \quad (8-60)$$

For the special case when there is no volume change on mixing at constant temperature at any pressure in the range from 0 to p , the partial molal volume of each component is equal to the pure-component molal volume and $\bar{z}_j = z_j$ at all pressures considered. Under these conditions and for p^* chosen as zero,

$$\ln \tilde{f}_j = \ln y_j + \ln f_j \quad (8-122)$$

$$\text{or} \quad \tilde{f}_j = y_j f_j \quad (8-123)$$

This is the *Lewis and Randall fugacity rule*, and it applies to ideal solutions. It is applicable to gases over a wider range than the perfect-gas law or Dalton's law employing partial pressures $p'_j = y_j p$. At pressures greater than 100 atm, serious deviations may be expected.

Equation (8-121) provides a rigorous basis for calculating the fugacity of a component in an actual mixture at high pressures whether the volumes are additive or not. This equation may be expressed more simply by letting p^* be zero and designating the resulting integral on the right as $\ln \bar{\phi}_j$, where $\bar{\phi}_j$ is called the *fugacity coefficient* for component j in a mixture. Then

$$\ln \bar{\phi}_j = \int_0^p \frac{\bar{z}_j - 1}{p} dp \quad (8-124)$$

With this substitution, Eq. (8-121) becomes

$$\tilde{f}_j = y_j \bar{\phi}_j p \quad (8-125)$$

and $\bar{\phi}_j$ may be evaluated when the information is available to carry out the integration in Eq. (8-124). The most accurate evaluation of $\bar{\phi}_j$ is likely to be obtained from an equation of state with several constants. Thus an excellent starting point for mixtures of hydrocarbons is the Benedict-Webb-Rubin equation of state. Charts and tables based on this equation have been prepared and are available,^{61,62} but these are too extensive for reproduction here. Two procedures will be described to supplement the information furnished by experimental data and by the Benedict-Webb-Rubin equation and to provide methods which may be applied to any substance and which require a minimum amount of data. The first employs the generalized charts based on the theorem of corresponding states, and the second uses the two-constant equation of state of Redlich and Kwong. The accuracy of both methods is limited by the failure of the theorem of corresponding states to be entirely precise. Both methods closely approach this inherent limit on their accuracy, but in use the latter method offers several practical advantages.

⁶¹ "Liquid-Vapor Equilibria in Mixtures of Light Hydrocarbons, MWK Equilibrium Constants, Polycy Data," The M. W. Kellogg Company, 1950.

⁶² C. L. DePriester, *Chem. Eng. Progr. Symposium Ser.*, **49**(7):1 (1953).

Fugacity Coefficients from Generalized Charts. The calculation of the fugacity coefficient for a component in a mixture may be carried out by using the generalized fugacity-coefficient charts given in Fig. 8-17a-c; the generalized enthalpy-pressure charts, Figs. 8-18 and 8-19; the generalized compressibility charts, Figs. 8-7 to 8-9; and the methods for calculating the pseudocritical temperature and the pseudocritical pressure. This method was proposed by Joffe.⁵⁶ The derivation for component 1 in a mixture of n components starts with the general equation for the partial molal volume of component 1 in the mixture. This is given by¹⁰

$$\bar{v}_1 = v + (1 - y_1) \frac{\partial v}{\partial y_1} - y_2 \frac{\partial v}{\partial y_2} - \cdots - y_{n-1} \frac{\partial v}{\partial y_{n-1}} \quad (8-126)$$

Both sides may be multiplied by dp and integrated from a low pressure approaching zero to the pressure of the mixture. From the definition of the fugacity coefficient $\bar{\phi}_1$ for component 1 in the mixture Eq. (8-124), the definition of the fugacity coefficient ϕ for the mixture considered as a single compound Eq. (8-60), and with some rearrangement, there results

$$\ln \bar{\phi}_1 = \ln \phi + (1 - y_1) \frac{\partial \ln \phi}{\partial y_1} - y_2 \frac{\partial \ln \phi}{\partial y_2} - \cdots - y_{n-1} \frac{\partial \ln \phi}{\partial y_{n-1}} \quad (8-127)$$

The partial derivatives of $\ln \phi$ with respect to y_1, y_2 , etc., may be evaluated by considering the fugacity coefficient a function of $T, p, y_1, \dots, y_{n-1}$. H. C. Van Ness and R. H. Bretton have developed the following rigorous method for evaluating the terms $\partial \ln \phi / \partial y_1, \partial \ln \phi / \partial y_2$, etc. Since $\ln \phi = \phi(T, p, y_1, y_2, \dots, y_{n-1})$

$$\begin{aligned} d \ln \phi = & \left(\frac{\partial \ln \phi}{\partial T} \right)_{p, y_1, \dots} dT + \left(\frac{\partial \ln \phi}{\partial p} \right)_{T, y_1, \dots} dp \\ & + \left(\frac{\partial \ln \phi}{\partial y_1} \right)_{T, p, y_2, \dots} dy_1 + \cdots \end{aligned} \quad (8-127a)$$

dT and dp in Eq. (8-127a) may be replaced by differentiating the expressions

$$\begin{aligned} T &= f(T_R, y_1, y_2, \dots, y_{n-1}) \\ \text{and} \quad p &= f'(p_R, y_1, y_2, \dots, y_{n-1}) \end{aligned}$$

The result contains terms multiplied by $dT_R, dp_R, dy_1, dy_2, \dots, dy_{n-1}$. This may be compared with a similar expression obtained by differentiating the generalized correlation $\ln \phi = f''(T_R, p_R)$. It is then evident that all the terms multiplied by $dy_1, dy_2, \dots, dy_{n-1}$ must vanish and that

$$\left(\frac{\partial \ln \phi}{\partial T_R}\right)_{p_R} = \left(\frac{\partial \ln \phi}{\partial T}\right)_{p, y_1, \dots} \left(\frac{\partial T}{\partial T_R}\right)_{y_1, \dots} \quad (8-128)$$

and

$$\left(\frac{\partial \ln \phi}{\partial p_R}\right)_{T_R} = \left(\frac{\partial \ln \phi}{\partial p}\right)_{T, y_1, \dots} \left(\frac{\partial p}{\partial p_R}\right)_{y_1, \dots} \quad (8-128a)$$

Also, from the generalized correlation,

$$\left(\frac{\partial \ln \phi}{\partial y_1}\right)_{T, p, y_2, \dots} = \left(\frac{\partial \ln \phi}{\partial T_R}\right)_{p_R} \left(\frac{\partial T_R}{\partial y_1}\right)_{T, p, y_2} + \left(\frac{\partial \ln \phi}{\partial p_R}\right)_{T_R} \left(\frac{\partial p_R}{\partial y_1}\right)_{T, p, y_2, \dots} \quad (8-128b)$$

Combining Eqs. (8-128), (8-128a), and (8-128b),

$$\begin{aligned} \left(\frac{\partial \ln \phi}{\partial y_1}\right)_{T, p, y_2, \dots} &= \left(\frac{\partial \ln \phi}{\partial T}\right)_{p, y_1, \dots} \left(\frac{\partial T}{\partial T_R}\right)_{y_1, \dots} \left(\frac{\partial T_R}{\partial y_1}\right)_{T, p, y_2, \dots} \\ &+ \left(\frac{\partial \ln \phi}{\partial p}\right)_{T, y_1, \dots} \left(\frac{\partial p}{\partial p_R}\right)_{y_1, \dots} \left(\frac{\partial p_R}{\partial y_1}\right)_{T, p, y_2, \dots} \end{aligned} \quad (8-129)$$

The terms on the right of Eq. (8-129) may be replaced as follows,

$$\left(\frac{\partial \ln \phi}{\partial T}\right)_{p, y_1, \dots} = \frac{H^* - H}{RT^2} \quad (8-130)^{10}$$

From the pseudocritical temperature and pressure proposed by Kay,

$$T'_c = y_1 T_{c_1} + y_2 T_{c_2} + \dots + (1 - y_1 - y_2 - \dots - y_{n-1}) T_{c_n} \quad (8-131)$$

$$p'_c = y_1 p_{c_1} + y_2 p_{c_2} + \dots + (1 - y_1 - y_2 - \dots - y_{n-1}) p_{c_n} \quad (8-131a)$$

it follows that

$$\left(\frac{\partial T_R}{\partial y_1}\right)_{T, p, y_2, \dots} = -\frac{T}{(T'_c)^2} (T_{c_1} - T'_{c_n}) \quad (8-131b)$$

and

$$\left(\frac{\partial p_R}{\partial y_1}\right)_{T, p, y_2, \dots} = -\frac{p}{(p'_c)^2} (p_{c_1} - p_{c_n}) \quad (8-131c)$$

From $T = T'_c T_R$ and $p = p'_c p_R$,

$$\left(\frac{\partial T}{\partial T_R}\right)_{y_1, \dots} = T'_c \quad \left(\frac{\partial p}{\partial p_R}\right)_{y_1, \dots} = p'_c \quad (8-132)$$

and also

$$\left(\frac{\partial \ln \phi}{\partial p}\right)_{T, y_1, \dots} = \frac{z - 1}{p} \quad (8-133)$$

Substituting Eqs. (8-130), (8-131b), (8-131c), (8-132), and (8-133) into Eq. (8-129) leads to

$$\left(\frac{\partial \ln \phi}{\partial y_1}\right)_{T, p, y_2, \dots} = \frac{H^* - H}{RT} \frac{T_{c_n} - T_{c_1}}{T'_c} + (z - 1) \frac{p_{c_n} - p_{c_1}}{p'_c} \quad (8-134)$$

Equation (8-134) and similar expressions for the partial derivatives with respect to y_2 , etc., are substituted in Eq. (8-127), and there results

$$\ln \bar{\phi}_1 = \ln \phi + \frac{H^* - H}{RTT'_c} (T'_c - T_{c1}) + \frac{(z - 1)(p'_c - p_{c1})}{p'_c} \quad (8-135)$$

Similar equations may be written for the fugacity coefficients of the other components. $H^* - H$ represents the difference in molal enthalpy of the mixture at a pressure low enough for it to behave as a perfect gas and at the pressure where $\bar{\phi}_1$ is to be evaluated, both at the same temperature. The first step in calculating $\bar{\phi}_1$ is to evaluate p'_c and T'_c by Eqs. (8-131) and (8-131a). These values and p and T are used to determine the pseudo-reduced pressure and the pseudoreduced temperature which permit determination of values of ϕ , $(H^* - H)/T_c$, and z from the generalized charts. These are then substituted into Eq. (8-135).

This method has been used to calculate the fugacities for mixtures of argon and ethylene to 125 atm, for mixtures of nitrogen and hydrogen to 600 atm, and for the ammonia-synthesis mixture at equilibrium to 1,000 atm. In the first two cases, the average deviation from measured values did not exceed about 3 per cent compared to average deviations of 6 and 7 per cent based on the Lewis and Randall fugacity rule. In the latter case, the average deviation at 1,000 atm was 4.2 per cent compared to 41.0 per cent for values calculated from the Lewis and Randall fugacity rule.

Fugacity Coefficient from Equation of State. The Redlich and Kwong equation of state (8-17) has been adapted⁶³ for use in calculating the fugacity coefficient for a component in a mixture. The constants for the equation of state for the mixture are obtained from the constants for the pure components according to Eq. (8-114) from the critical temperature and critical pressure of each component and the temperature of the mixture. The partial molal compressibility coefficient for one component may be expressed in terms of the equation of state, and this result is substituted in Eq. (8-124). An equation for $\bar{\phi}_j$ is obtained as follows.

$$\log \bar{\phi}_j = \log \phi' - u \left(\frac{A_j}{A} - 1 \right) + w \left(\frac{B_j}{B} - 1 \right) \quad (8-136)$$

$$\text{Here} \quad \log \phi' = 0.4343(z - 1) - \log(z - Bp) - \frac{A^2}{B} \log \left(1 + \frac{Bp}{z} \right) \quad (8-137)$$

$$u = 2 \frac{A^2}{B} \log \left(1 + \frac{Bp}{z} \right) \quad (8-138)$$

$$w = 0.4343(z - 1) + \frac{A^2}{B} \log \left(1 + \frac{Bp}{z} \right) \quad (8-139)$$

⁶³ O. Redlich, A. T. Kister, and C. E. Turnquist, *Chem. Eng. Progr. Symposium Ser.*, **48**(2):49 (1952).

Since z is a function of A and B , the right-hand side of each of Eqs. (8-137), (8-138), and (8-139) may be represented as a function of Bp and A^2/B . These relationships are shown in Figs. 8-47 to 8-49, where $\log \phi'$, u , and w are plotted as functions of Bp and A^2/B . A table of the values used to prepare these three figures is given in Appendix B. The table assists in interpolation and extrapolation and also lists values for z .

Liquid Solutions, Nonelectrolytes. The effect of pressure on liquid solutions in low and intermediate pressure ranges is not so pronounced as the effect on gases. However, this effect is appreciable and often should not be neglected. The interaction of one component on another, on the other

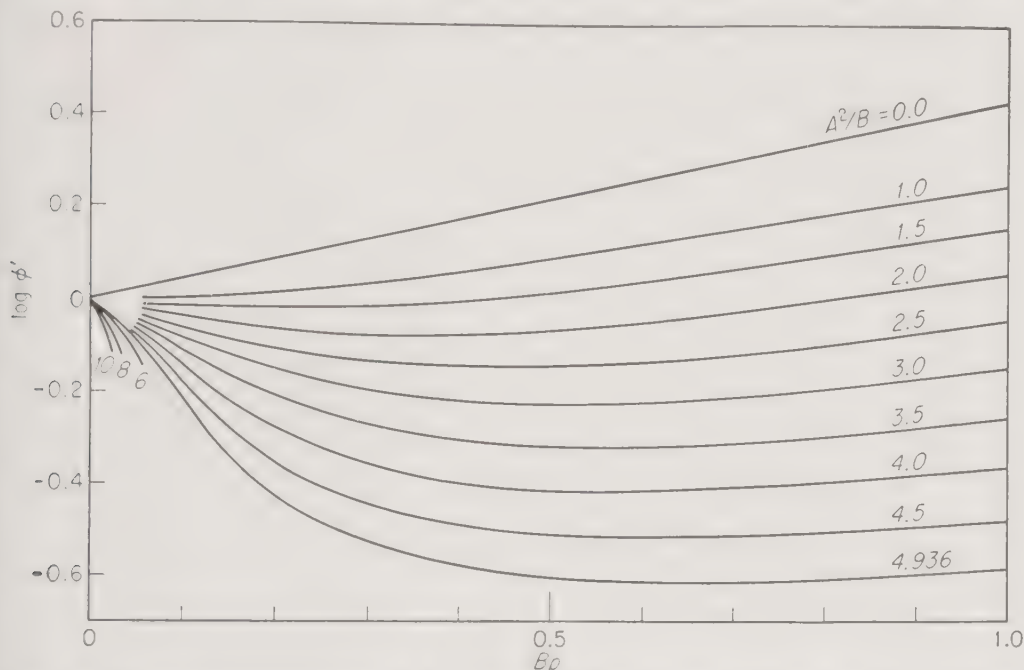


FIG. 8-47. Chart for calculation of $\bar{\phi}_i$. [From O. Redlich, A. T. Kister, and C. E. Turnquist, *Chem. Eng. Progr. Symposium Ser.*, **48**(2):49 (1952).]

hand, is more pronounced and varies over greater ranges in liquids than in gases. Both these effects must be taken into account by any method for predicting the phase equilibrium between a liquid solution and a gas or vapor mixture. In considering the behavior of a liquid solution, it is convenient to use the activity and the activity coefficient. Lewis and Randall²¹ defined the activity of a component as the ratio of the fugacity of the component in solution to its fugacity as a pure liquid. Thus, at a given temperature and total pressure,

$$\bar{a}_1 = \frac{\bar{f}_1}{f_1} \quad \text{and} \quad \bar{a}_2 = \frac{\bar{f}_2}{f_2} \quad (8-140)$$

where \bar{a}_1 and \bar{a}_2 = activities of components 1 and 2 in the solution
 \bar{f}_1 and \bar{f}_2 = fugacities of components 1 and 2 in solution
 f_1 and f_2 = fugacities of components 1 and 2 as pure liquids

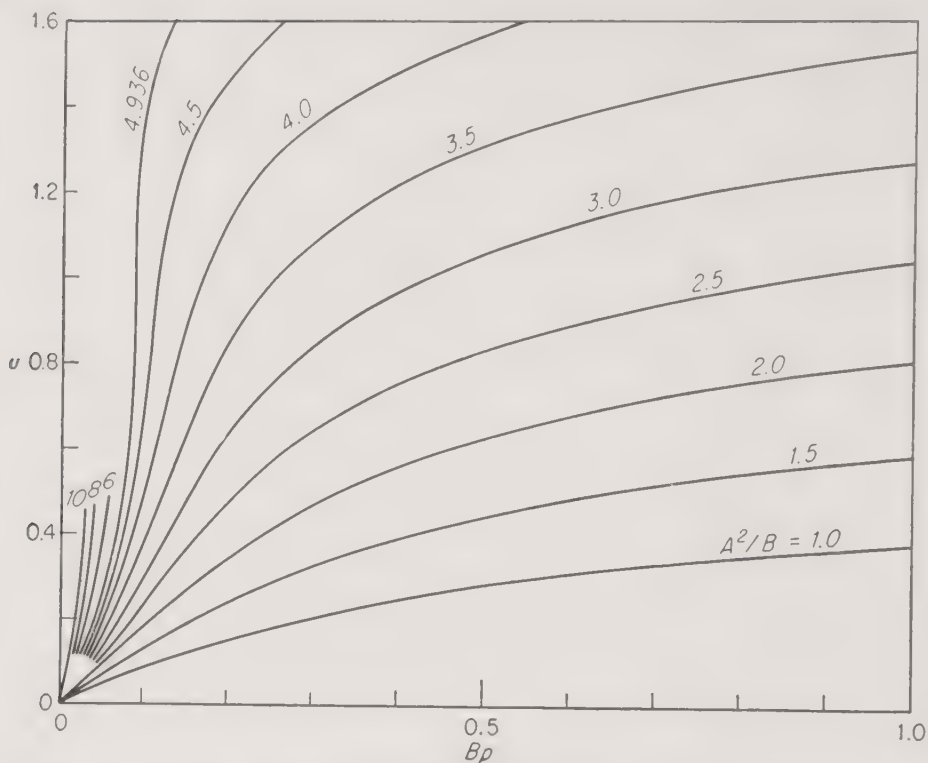


FIG. 8-48. Chart for calculation of $\bar{\phi}_1$. [From O. Redlich, A. T. Kister, and C. E. Turnquist, *Chem. Eng. Progr. Symposium Ser.*, **48**(2):49 (1952).]

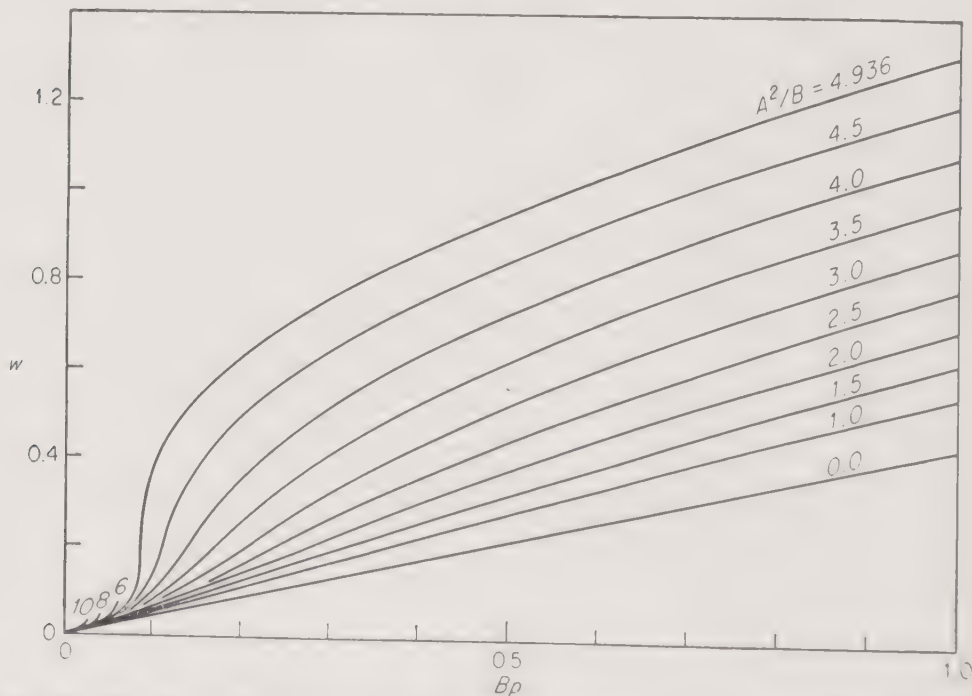


FIG. 8-49. Chart for calculation of $\bar{\phi}_1$. [From O. Redlich, A. T. Kister, and C. E. Turnquist, *Chem. Eng. Progr. Symposium Ser.*, **48**(2):49 (1952).]

The activity coefficient γ is defined as the ratio of the activity of a component to its mole fraction in the solution. Thus

$$\gamma_1 = \frac{\bar{a}_1}{x_1} \quad \gamma_2 = \frac{\bar{a}_2}{x_2} \quad (8-141)$$

or

$$\gamma_1 = \frac{\bar{f}_1}{f_1 x_1} \quad \gamma_2 = \frac{\bar{f}_2}{x_2 f_2} \quad (8-142)$$

Gibbs-Duhem Equation. The most general form of the Gibbs equation⁶⁴ for two components in a homogeneous open system in equilibrium with another system is

$$v dp - S dT = n_1 d\mu_1 + n_2 d\mu_2 \quad (8-143)$$

where n_1 = number of moles of component 1 in the system

μ_1 = chemical potential of component 1, etc.

For a definition and discussion of chemical potential, the reader is referred to texts on thermodynamics.¹⁰ Equation (8-143) applies equally to the liquid phase and to the vapor phase. It will be applied to the liquid phase in the discussion which follows. It may be written in terms of the mole fractions in the liquid phase as

$$v dp - S dT = x_1 d\mu_1 + (1 - x_1) d\mu_2 \quad (8-144)$$

The fugacity is related to the chemical potential μ by relations of the type

$$d\mu_1 = d\bar{F}_1 = RT d \ln \bar{f}_1 = \bar{v}_1 dp \quad \text{at constant } T \quad (8-145)$$

When Eq. (8-144) is applied to a liquid in equilibrium with its own vapor, the phase rule indicates that it is possible to consider changes of composition and temperature at constant pressure or changes of composition and pressure at constant temperature, but it is not in general possible to change one of these variables while keeping the other two constant and at the same time maintain equilibrium between gas and liquid phases.

Equation (8-145) may be introduced into Eq. (8-144), and the following relation results.

$$x_1 d \ln \bar{f}_1 + (1 - x_1) d \ln \bar{f}_2 = \frac{v dp}{RT} \quad \text{at constant } T \quad (8-146)$$

where v is the molal volume of the mixture. Additional thermodynamic reasoning produces the equation

$$x_1 d \ln \bar{f}_1 + (1 - x_1) d \ln \bar{f}_2 = \frac{\Delta H}{RT^2} dT \quad \text{at constant } p \quad (8-147)$$

where $\Delta H = x_1 H_1^* + (1 - x_1) H_2^* - x_1 \bar{H}_1 - (1 - x_1) \bar{H}_2$ and is therefore the molal ideal heat of vaporization. This is the heat required to vaporize

⁶⁴ N. V. Ibl and B. F. Dodge, *Chem. Eng. Sci.*, **2**:120 (1953).

1 mole of the liquid mixture originally at p and T to a vapor at a pressure sufficiently low for the perfect-gas law to be valid.

Equations (8-146) and (8-147) may be expressed in terms of the activity coefficients. To do this we first choose as standard states the pure liquid components at the pressure and temperature of the solution. Then

$$\gamma_1 = \frac{\bar{f}_1}{x_1 f_1} \quad \gamma_2 = \frac{\bar{f}_2}{(1 - x_1) f_2} \quad (8-142)$$

where f_1 and f_2 are the fugacities of the pure liquids at the same temperature and pressure as the mixture. These values are introduced into Eqs. (8-146) and (8-147) and lead to the equations

$$x_1 d \ln \gamma_1 f_1 + (1 - x_1) d \ln \gamma_2 f_2 = \frac{v dp}{RT} \quad \text{at constant } T \quad (8-148)$$

$$\text{and} \quad x_1 d \ln \gamma_1 f_1 + (1 - x_1) d \ln \gamma_2 f_2 = \frac{\Delta H dT}{RT^2} \quad \text{at constant } p \quad (8-149)$$

The fugacities in the standard states f_1 and f_2 may be replaced by using Eqs. (8-55) and (8-145) and by relations of the type

$$d \ln f_1 = \frac{H_1^* - \bar{H}_1}{RT^2} dT \quad \text{at constant } p \text{ and } x \quad (8-150)$$

Then Eqs. (8-148) and (8-149) become

$$x_1 d \ln \gamma_1 + (1 - x_1) d \ln \gamma_2 = \frac{\Delta v' dp}{RT} \quad \text{at constant } T \quad (8-151)$$

$$\text{and} \quad x_1 d \ln \gamma_1 + (1 - x_1) d \ln \gamma_2 = \frac{\Delta H' dT}{RT^2} \quad \text{at constant } p \quad (8-152)$$

$\Delta v' = v - x_1 v_1 - (1 - x_1) v_2$ and is the volume change when a mole of mixture is prepared from the pure liquid components at T and p . $\Delta H' = x_1 \bar{H}_1 + (1 - x_1) \bar{H}_2 - x_1 H_1 - (1 - x_1) H_2$ and is the integral heat of mixing when 1 mole of mixture is prepared from the pure liquid components.

Equations (8-151) and (8-152) are general forms of Duhem's equations in terms of activity coefficients. For a mixture in a single phase, not in equilibrium with its own vapor, both temperature and pressure may be held constant, and under these conditions Eqs. (8-151) and (8-152) both become

$$x_1 d \ln \gamma_1 + (1 - x_1) d \ln \gamma_2 = 0 \quad \text{at constant } T \text{ and } p \quad (8-153)$$

This is a common form of the Duhem equation. For a two-component system where $dx_1 = -dx_2$, it may be put in the following form by dividing by dx_1 ,

$$x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2} \quad \text{at constant } T \text{ and } p \quad (8-153a)$$

Activity Coefficients in Liquid Mixtures. A knowledge of the activity coefficients will permit the calculation of the behavior of liquid solutions and is especially useful in predicting the composition of liquid and vapor phases in equilibrium. Empirical and semiempirical relations have been proposed to relate the activity coefficients to the mole fractions in the solution.

Margules proposed expressions for binary mixtures of the form⁶⁵

$$\ln \gamma_1 = ax_2 + bx_2^2 + cx_2^3 \quad (8-154)$$

$$\ln \gamma_2 = a'x_1 + b'x_1^2 + c'x_1^3 \quad (8-155)$$

By using the Eq. (8-153a), Margules' equations may be simplified to a form containing only two constants,⁵⁹

$$\ln \gamma_1 = bx_2^2 + cx_2^3 \quad (8-156)$$

$$\ln \gamma_2 = bx_1^2 + \frac{2}{3}cx_1^3 - cx_1^3 \quad (8-157)$$

Van Laar used a semitheoretical development and arrived at equations of the form

$$\ln \gamma_1 = \frac{B/T}{(1 + Ax_2/x_1)^2} \quad (8-158)$$

$$\ln \gamma_2 = \frac{AB/T}{(A + x_2/x_1)^2} \quad (8-159)$$

Other equations have been proposed by Scatchard and Hildebrand, by Clark, and by Redlich and Kister. The equations by Redlich and Kister are more flexible and may be adapted to systems of great or little complexity and to multicomponent systems.

Equations by Redlich and Kister. The first step⁶³ in the development of the relations between the activity coefficients and the composition is to define the function Q . Limiting the definition, at first, Q is defined by the equation

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 \quad (8-160)$$

Since $\gamma_1 = 1$ for $x_1 = 1$, and $\gamma_2 = 1$ for $x_2 = 1$, the function Q is zero at $x_1 = 1$ and $x_2 = 1$. It is zero at any concentration for the special case of an ideal solution. For actual solutions it is a function of the composition

⁶⁵ C. S. Robinson and E. R. Gilliland, "Elements of Fractional Distillation," 4th ed., McGraw-Hill Book Company, Inc., New York, 1950.

and the temperature. A general empirical equation to represent Q is

$$Q = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \cdots] \quad (8-161)$$

where the coefficients B , C , D , . . . depend on the temperature. The activity coefficients may then be found as follows. Total differentiation of Eq. (8-160) with respect to x_1 gives

$$\frac{dQ}{dx_1} = \log \gamma_1 - \log \gamma_2 + x_1 \frac{d \log \gamma_1}{dx_1} + x_2 \frac{d \log \gamma_2}{dx_1}$$

The last two terms cancel in view of Eq. (8-153a). When the remaining equation is multiplied first by x_2 and again by $-x_1$, we have the two equations

$$\log \gamma_1 = Q + x_2 \frac{dQ}{dx_1} \quad \log \gamma_2 = Q - x_1 \frac{dQ}{dx_1} \quad (8-162)$$

Carrying out the indicated operations on Eq. (8-161) leads to

$$\log \gamma_1 = x_2^2 [B + C(3x_1 - x_2) + D(x_1 - x_2)(5x_1 - x_2) + E(x_1 - x_2)^2(7x_1 - x_2) + \cdots] \quad (8-163)$$

$$\log \gamma_2 = x_1^2 [B + C(x_1 - 3x_2) + D(x_1 - x_2)(x_1 - 5x_2) + E(x_1 - x_2)(x_1 - 7x_2) + \cdots] \quad (8-164)$$

The quantity $\log (\gamma_1/\gamma_2)$ is useful in most applications.

$$\begin{aligned} \log \frac{\gamma_1}{\gamma_2} &= \frac{dQ}{dx_1} = B(-x_1 + x_2) + C(-1 + 6x_1 x_2) \\ &\quad + D(x_1 - x_2)(-1 + 8x_1 x_2) + E(x_1 - x_2)^2(-1 + 10x_1 x_2) + \cdots \end{aligned} \quad (8-165)$$

Integration of Eq. (8-165) provides a basis for determining whether experimental measurements are thermodynamically consistent. Since Q is zero for both $x_1 = 0$ and $x_1 = 1$, it follows that

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (8-165a)$$

If $\log (\gamma_1/\gamma_2)$ is plotted against x_1 , the area above the abscissa must equal that below. This "area condition" applies strictly only at constant temperature but may be used in practice over a small temperature interval.

In using the series shown by Eq. (8-161), only as many coefficients B , C , D , . . . are evaluated as are required to represent the behavior of the system. For systems which are adequately represented by the Margules or Van Laar equations, two terms in Eq. (8-161) will suffice. This method of representation is then no more complex than the methods based on equations with two coefficients. Systems requiring additional coeffi-

cients are adequately represented by using additional terms in Eq. (8-161).

Only the first term is required for nearly ideal solutions such as *n*-hexane-toluene. Two terms are sufficient for benzene-2,2,3-trimethylbutane. A third term is necessary for solutions containing an associating component such as an alcohol or an acid. Four terms are seldom required and then only when very accurate measurements are available or for extremely nonideal solutions such as ethanol-methylcyclohexane. A number of conclusions as to the influence of association among the components on the coefficients are given by Redlich, Kister, and Turnquist,⁶³ and Scatchard⁶⁶ has derived a theory for associated solutions.

In extending the representation to multicomponent systems, the activity coefficients in the multicomponent system can be estimated if the coefficients *B*, *C*, etc., for the binary systems involved are known. For a multicomponent system, the function *Q* is defined by

$$Q = \sum_j x_j \log \gamma_j \quad (8-166)$$

In place of Eq. (8-161), the function *Q* is then represented by the sum of the series of equations of the form of Eq. (8-161) which can be written for all binary combinations which can be prepared from the components of the systems plus terms for the interaction of three, four, etc., different-component molecules. These latter terms are determined by measurements on the various combinations of ternary, quaternary, etc., systems which can be prepared from the components. However, if all the components are miscible, these latter terms may be neglected in estimating the activity coefficients. The approximate relation is then

$$Q = \sum_{i,j} x_i x_j [B_{ij} + C_{ij}(x_i - x_j) + \cdots] \quad i \neq j \quad (8-167)$$

where the summation is of all possible combinations of *i* and *j* for the *n* components but omitting the terms for *i* = *j*. The activity coefficients are determined from Eq. (8-167) by means of the binary coefficients *B*_{*ij*}, etc., by applying it in the thermodynamic relation

$$\log \gamma_r = Q + \frac{\partial Q}{\partial x_r} - \sum_k x_k \frac{\partial Q}{\partial x_k} \quad (8-168)$$

In the partial differentiations, all mole fractions are kept constant except the one indicated by the subscript on *x*. The calculations in actual cases

⁶⁶ G. Scatchard, *Chem. Revs.*, **44**:7 (1949).

are much simpler than indicated by the general case since only a few of the terms in Eq. (8-167) are used.

8-17. Vapor-Liquid Equilibrium. The definition of the activity coefficient by Eqs. (8-141) and (8-142) is that originally proposed by Lewis and Randall. According to this definition, the activity coefficient is a function of both composition and pressure at any fixed temperature. Redlich, Kister, and Turnquist⁶³ have shown that the application of the activity coefficient to liquid solutions is considerably simplified and the thermodynamic derivations are clarified if the activity coefficient is defined in such a way that it is independent of the pressure. The activity coefficient defined in this manner will be designated γ'_i . This redefined activity coefficient will be limited to use with liquids. It will be applicable at only one constant pressure p_s , usually chosen as 1 atm. The effect of pressure changes on the fugacity of the components in the liquid is evaluated separately and is not accounted for in the activity coefficient. The activity coefficient is then independent of pressure. The logarithm of the fugacity of the i th component in a liquid solution under the pressure p is given by

$$\ln \bar{f}_i = \ln x_i \gamma'_i k_i + \int_{p_s}^p \frac{\bar{v}_i}{RT} dp \quad \text{at constant } T \quad (8-169)$$

Here k_i is a constant to be determined by the convention adopted regarding the standard state for the liquid. The value of k_i is determined as follows.

At equilibrium between the vapor and the liquid, the fugacity \bar{f}_i and thus the logarithm of the fugacity $\ln \bar{f}_i$ for any component i has the same value in both phases. Therefore,

$$\ln x_i \gamma'_i k_i + \int_{p_s}^p \frac{\bar{v}_i}{RT} dp = \ln y_i \bar{\phi}_i p \quad (8-170)$$

According to the usual conventions, $\gamma'_i = 1$ for the pure component $x_i = 1$. Under these conditions, the equilibrium pressure p is the vapor pressure P_i , $y_i = 1$, and k_i is determined by substituting these values in Eq. (8-170).

$$\ln k_i + \int_{p_s}^{P_i} \frac{\bar{v}_i}{RT} dp = \ln \phi_i P_i \quad (8-171)$$

where ϕ_i is the fugacity coefficient for the pure vapor at its vapor pressure at temperature T .

The condition for vapor-liquid equilibrium is now expressed by

$$\ln K_i = \ln \frac{y_i}{x_i} = \ln \frac{\gamma'_i \phi_i P_i}{\bar{\phi}_i p} + \int_{P_i}^p \frac{\bar{v}_i}{RT} dp \quad (8-172)$$

It is convenient to define a new term, the *adjusted vapor pressure* P'_i , by the relation

$$\ln P'_i = \ln \frac{P_i \phi_i}{\bar{\phi}_i} + \int_{P_i}^p \frac{\bar{v}_i}{RT} dp \quad (8-173)$$

By introducing Eq. (8-173) into Eq. (8-172), there results

$$K_i = \frac{y_i}{x_i} = \frac{\gamma'_i P'_i}{p} \quad (8-174)$$

The adjusted vapor pressure is a convenient term and may be substituted for the vapor pressure in many equations which are valid for perfect gases or at low pressures. The resulting expression may then be used at high pressures. As an example, the total pressure of a vapor in equilibrium with a liquid solution is

$$p = p \sum y_i = \sum x_i \gamma'_i P'_i \quad (8-175)$$

The term P'_i may be evaluated by an approximate relation with sufficient accuracy for most purposes except in the region in the neighborhood of the critical state. Except in the critical region, the partial molal volume \bar{v}_i is approximately v_i , the molal volume of the pure liquid component, and the integral in Eq. (8-173) may be expressed as $v_i(p - P_i)/RT$. The approximate form of Eq. (8-173) is then

$$\ln P'_i = \ln \frac{P_i \phi_i}{\bar{\phi}_i} + \frac{v_i(p - P_i)}{RT} \quad (8-176)$$

NOMENCLATURE

- A Compressibility factor $pV/p_s V_s$; parameter in Eq. (8-20); cross sectional area
- A_0 Constant in Eqs. (8-29) and (8-30)
- a Constant in Eqs. (8-5), (8-17), (8-24), (8-27), (8-29), (8-30), and (8-45)
- \bar{a}_1 Activity coefficient of component 1 in a liquid solution; \bar{a}_2 for component 2, etc.
- B Parameters in Eqs. (8-20), (8-30), and (8-161); constant in Eq. (8-80)
- B_0 Constant in Eq. (8-29)
- b Constant in Eqs. (8-5), (8-17), (8-24), (8-27), (8-29), (8-30), and (8-45)
- C Constant in Eq. (8-80); parameter in Eq. (8-32a); parameter in Eq. (8-161)
- C Number of components in a system
- C_0 Constant in Eq. (8-30)
- C_p Molal heat capacity at constant pressure; c_p , specific heat
- C_p^* Molal heat capacity at constant pressure at low pressure
- c Constant in Eqs. (8-29), (8-30), and (8-45); concentration in a mixture; number of molecules per unit volume [in Eq. (8-99)]
- c_1 Concentration of component 1, g moles/liter; c_2 for component 2

- c_m Molal density of a gas mixture, g moles/liter
- D Diameter of tube; parameter in Eq. (8-161)
- D_{12} Molecular diffusivity of molecular species 1 through species 2; D_0 , a constant in Eq. (8-98) which is a function of density
- d Molal density ρ/M
- E Molal internal energy; parameter in Eq. (8-161)
- \mathcal{E} Activation energy
- F Molal free energy $E + pv - TS$
- F_i Free energy of an ideal gas at p and T corresponding to p_R and T_R
- \bar{F}_j Partial molal free energy of component j in the mixture,
 $(\partial F/\partial n_j)_{T,p,n_1,n_2,\dots,n_i,\dots,i \neq j}$
- f Fugacity, atm
- f° Fugacity in the standard state or at pressure p°
- f^* Fugacity at T and p^*
- \bar{f}_j Fugacity of component j in a mixture; \bar{f}_1 for component 1, etc.
- g Intercept at $T = 0$ of straight isometric
- H Molal enthalpy $E + pv$
- H^* Enthalpy at T and p^*
- h $Bp/z = p/v$ [see Eq. (8-23)]
- I Cohesive pressure or internal pressure, atm
- K_i Phase-equilibrium constant y_i/x_i
- k Thermal conductivity $\frac{dq/A}{dt/dx} \frac{d\theta}{dx}$; k_1 is value at atmospheric pressure
- L The available distance between molecules
- \ln Natural logarithm
- \log Logarithm to the base 10
- M Molecular weight
- N_1 Rate of mass transfer of component 1
- n Number of moles; n_A = moles of A, etc.; constant exponent in Eq. (8-45); variable exponent in Eq. (8-67)
- \mathcal{O} Number of phases
- P_i Vapor pressure of a pure substance i
- P'_i Adjusted vapor pressure defined by Eq. (8-173)
- p Total pressure, atm
- p° Pressure of gas corresponding to a standard state at low pressure where the perfect-gas law applies
- p_i Pressure RT/v of a perfect gas at the temperature T and molal volume v
- p_c Critical pressure
- p'_c Pseudocritical pressure [see Eq. (8-110)]
- p''_c Pseudocritical pressure [see Eqs. (8-112) and (8-113)]
- p_s Pressure at standard conditions, usually 1 atm
- p_k Kinetic pressure, atm
- p^* A pressure sufficiently low that the gas acts as a perfect gas; $p_j^* = y_j p^*$
- p' Approximate pressure obtained from the equation for a straight isometric
- p_R Reduced pressure, p/p_c
- p_v Maximum pressure on the border curve at a constant composition

- p_A Pure-component pressure of component A in a vapor; p_B of component B, etc.
 p'_A Partial pressure of component A in a vapor mixture defined as $y_A p$
 p''_A Partial pressure of component A in a vapor mixture defined as $y_A \bar{p}_A$
 \bar{p}_A Pressure of A alone at the same molal concentration as A and B combined in a vapor mixture
 Q Quantity defined by Eqs. (8-160) and (8-166)
 q Quantity of heat, Btu
 R Gas-law constant
 r_0 Collision diameter of the molecules
 r_1 First residual $p - p'$
 r'_1 Approximate value of first residual obtained from Eq. (8-45)
 r_2 Second residual $r'_1 - r_1$
 S Molal entropy
 S_i Molal entropy of an ideal gas at p and T corresponding to p_R and T_R
 S^* Molal entropy at T and p^*
 s Slope of the straight isometric line for a single phase
 T Absolute temperature
 T_c Critical temperature
 T'_c Pseudocritical temperature [see Eq. (8-110)]
 T''_c Pseudocritical temperature [see Eqs. (8-112) and (8-113)]
 T_R Reduced temperature T/T_c
 T_l Maximum temperature on the border curve at a constant composition
 T_0 Boiling point at atmospheric pressure
 t Temperature, °F or °C
 U Average velocity
 U_s Velocity of sound in a liquid
 u Local velocity
 \mathcal{V} Number of independent variables
 V Total volume nv
 V_s Total volume at standard conditions of 1 atm and 0°C
 v Molal volume
 v'_R Ideal reduced volume, $v/(RT_c/p_c)$
 v_c Critical molal volume
 \bar{v}_j Partial molal volume of the j th component in a mixture,

$$\left(\frac{\partial V}{\partial n_j} \right)_{T, p, n_1, n_2, \dots, n_i, \dots} \quad i \neq j$$

- X Collision probability factor in Eq. (8-27)
 \mathfrak{X} Term defined for Eq. (8-99)
 x Mole fraction; distance measured in direction parallel to direction of heat flow, or molecular diffusion
 x_A Mole fraction in the liquid of component A; x_B of component B, etc.
 y Distance measured in a direction normal to the direction of flow
 y_A Mole fraction of component A in the vapor; y_B of component B, etc.
 z Compressibility factor pv/RT

- α A residual $RT/p - v$; constant in Eq. (8-30); coefficient of thermal expansion $\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p$; thermal diffusion ratio in Eq. (8-100); α_0 at low pressure where gas is a perfect gas
- β A residual $v/RT - 1/p = (z - 1)/p$; constant in Eq. (8-3); the compressibility $-\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T$
- γ Constant in Eqs. (8-3), (8-30); activity coefficient $\gamma_1 = \bar{a}_1/x_1 = \bar{f}_1/f_1x_1$, etc.
- γ'_i Redefined activity coefficient for component i in liquids $y_i p/x_i P'_i$
- θ Time
- ΔH_v Latent heat of vaporization of a liquid at its normal boiling point
- μ Viscosity
- μ_i Viscosity at a low pressure where the gas acts as a perfect gas. At 1 atm this is designated μ_1
- μ_i Chemical potential for component i in a mixture $(\partial F/\partial n_i)_{p,T,n_j} (j \neq i)$
- ρ Density, lb/cu ft
- σ Collision diameter for solid elastic spheres—assumed equal to r_0
- τ Unit shearing stress, force per unit area
- v Reduced mass
- ϕ Fugacity coefficient f/p
- φ_1 Correction factor given by Eq. (8-67)
- φ'' Collision-cross section integral
- $\bar{\phi}_j$ Fugacity coefficient for component j in a mixture [see Eqs. (8-124) and (8-125)]
- ω Expansion factor for liquids $\rho T_c/Mp_c$

CHAPTER 9

CHEMICAL-ENGINEERING UNIT OPERATIONS

Manufacturing processes which include a chemical change usually consist of a series of steps. These steps may be separate batch operations, but more often they are continuous operations in an integrated chemical-manufacturing plant. Some of these operations are chiefly physical in nature. The material in process is heated or cooled, conducted through pipes or metering systems, separated into components by distillation, absorption, or adsorption, and the like. These are known as chemical-engineering unit operations. The number of such operations carried out under elevated pressure is small. Nevertheless, a knowledge of the effect of pressure on the chemical-engineering unit operations is of importance.

The effect of pressure on these operations can usually be anticipated and sometimes accurately predicted if the behavior of the fluid under pressure is known or predictable. Thus, a knowledge of the effect of pressure on the physical and thermal properties, pVT relations, phase behavior, and the like, of a fluid is of principal importance. Such knowledge is more generally useful and has been given more attention by investigators than has the determination of the effect of pressure on the unit operations. A few quantitative investigations of the effect of pressure on individual unit operations have been performed.

9-1. Heat Transfer. Heat transfer will be divided into two cases—that for a single fluid phase and that for two phases when boiling occurs.

Single-phase Fluid. The methods used to determine the heat-transfer surface required to handle a given thermal load under ordinary pressure conditions may also be used under high-pressure conditions. Care must be exercised to select the correlations or equations which include the pertinent physical properties most likely to change with pressure.

Heat-transfer coefficients were measured by Colburn, Drew, and Worthington¹ for a 3:1 hydrogen-nitrogen mixture flowing through a 5-ft length of $\frac{5}{8}$ -in.-ID steel tubing at pressures from 30 to 900 atm. The range of Reynolds numbers extended from 40,000 to the unusually high value of 440,000. The coefficients they measured are shown in

¹ A. P. Colburn, T. B. Drew, and Hood Worthington, *Ind. Eng. Chem.*, **39**:958 (1947).

Fig. 9-1. These extend to 1000 $\text{Pcu}/(\text{hr})(\text{sq ft})(^\circ\text{C})$ at a mass velocity of 500,000 $\text{lb}/(\text{hr})(\text{sq ft})$. This mass velocity would require a linear velocity of the order of 5,000 ft/sec for the same gas at atmospheric pressure. Such a velocity is normally not attainable. At 900 atm, the linear velocity is of the order of 5 ft/sec, which is reasonable compared to velocities usually specified in design calculations. The increase in density is the major effect permitting operation at much higher mass

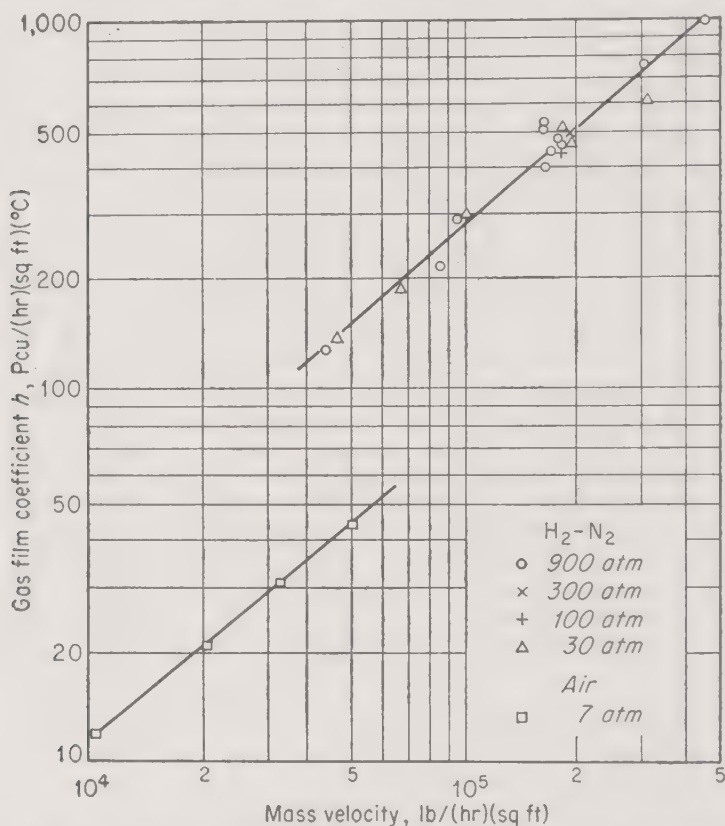


FIG. 9-1. Gas-film heat-transfer coefficients for 3:1 hydrogen-nitrogen mixture under high pressure. [From A. P. Colburn, T. B. Drew, and H. Worthington, *Ind. Eng. Chem.* **39**:958 (1947).]

velocities and consequently higher heat loads per unit of heat-transfer surface. Also shown in Fig. 9-1 are coefficients from the same apparatus for air at 7 atm. These are not on the same line as for the nitrogen-hydrogen mixtures. The experiments on air may be brought into good agreement with those for the hydrogen-nitrogen mixture by dividing the coefficients by the specific heat of each gas. The ratio of the heat-transfer coefficient to the specific heat then falls on a single line when plotted vs. mass velocity. The authors conclude that for nonviscous fluids inside pipes without calming sections the equation

$$j = \frac{h}{c_p G} \varphi = 0.023 \left(\frac{DG}{\mu} \right)^{-0.2} \quad (9-1)$$

is suitable, although it is likely to be conservative at low Reynolds numbers in the vicinity of 10,000. The measurements thus fit the equations based on a "j" factor $h/c_p G \varphi$. Boelter, Martinelli, and Jonassen² have proposed expressions for evaluating φ . φ depends on the Prandtl number N_{Pr} and to a slight extent on the Reynolds number N_{Re} and for the conditions of these tests was found to have a value of 1.42 at from 30 to 300 atm and 1.45 at 900 atm. The j factor as defined above is predicted to be one-half the friction factor f in the Fanning equation, or

$$\frac{h}{c_p G} \varphi = \frac{f}{2} \quad (9-2)$$

The friction factor may be obtained from the equation by Drew, Koo, and McAdams,³

$$\frac{f}{2} = 0.00070 - 0.0625 \left(\frac{DG}{\mu} \right)^{-0.32} \quad (9-3)$$

The measurements by Colburn, Drew, and Worthington were made at relatively high reduced temperatures (that is, T/T_c) for the gases used. Under these conditions, marked changes in viscosity, thermal conductivity, and heat capacity with pressure are not experienced. The effect of changes in these properties with pressure will be more pronounced at values of the reduced temperature nearer to unity. Measurements in this range have recently been made by Bringer.^{3a} A knowledge of the variation of the fluid properties near the critical point should permit the prediction of the variation in the heat-transfer coefficients with pressure near the critical. Because of the marked tendency for convection at the critical point, measurements in this region may show unusual behavior.

The local coefficients of heat transfer to superheated steam under pressure have been measured by McAdams, Kennel, and Addoms.⁴ The steam flowed upward in a vertical annulus and received heat from a 12.3-in. length of 0.252-in. tubing. The pressures covered a range from 115 to 3,500 psia for temperatures from 430 to 1000°F. The measured coefficients were correlated by the equation

$$\frac{(h D_e / k_f)^{1/3} \left(\frac{L}{D_e} \right)^{0.13}}{(c_p \mu / k)_f} = 0.0126 \left(\frac{DG}{\mu_f} \right)^{0.89} \quad (9-4)$$

² L. M. K. Boelter, R. C. Martinelli, and F. Jonassen, *Trans. ASME*, **63**:447 (1941).

³ T. B. Drew, E. C. Koo, and W. H. McAdams, *Trans. Am. Inst. Chem. Engrs.*, **28**:56 (1932).

^{3a} R. P. Bringer, "Heat Transfer to Fluids with Variable Properties; Carbon Dioxide in the Critical Region," Ph.D. thesis, Purdue University, Lafayette, Ind., 1956.

⁴ W. H. McAdams, W. E. Kennel, and J. M. Addoms, *Trans. ASME*, **72**:421 (1950).

No experiments have been described for the flow of fluids outside tubes either parallel or normal to the tubes. Nevertheless, it is to be expected that the design methods which apply to these cases at lower pressures⁵ will also apply at high pressure if account is taken of the effect of pressure on the pertinent properties of the fluids.

Natural Convection. A fluid in an enclosure will remain at rest (except for the normal molecular motion) as to bulk movement of any portion if temperature, pressure, density, and like properties are uniform throughout the fluid. A variation in temperature, for instance, from one point to another (a temperature gradient) is likely to result in a variation in density. If a heavy portion of the fluid is higher than a lighter portion, the one will sink and the other rise as a bulk movement of fluid. This is termed natural convection. pVT and phase-equilibrium measurements are made under uniform conditions, and convection is not a problem. On the other hand, the transport properties of thermal conductivity, molecular diffusivity, and the like, are measured in the presence of gradients of temperature, concentration, etc., and these gradients will induce convection unless special precautions are taken. The tendency for convection to occur varies with the properties of the fluid, and these vary with pressure.

When a fluid is confined between parallel walls, the walls exert a stabilizing effect tending to prevent convection. This effect is inversely proportional to the cube of the distance between the walls, and under certain conditions a very narrow space is required when convection must be avoided. Kraussold⁶ examined the results of a number of investigators on heat transfer through stagnant gas layers and included results of his own on water and oils. Most of these results applied to annular spaces, both in vertical and horizontal positions. Some of the data were from gases in horizontal gas layers. Kraussold expressed the measured heat-transfer rate in terms of an apparent or fictitious thermal conductivity k_a which included heat transfer by convection. The ratio of this apparent conductivity to the true conductivity was then found to be a function of the product of the Grashof and Prandtl numbers when this product was greater than 600. Below 600 the apparent and true conductivities were equal (indicating the absence of convection) and were independent of the Grashof- and Prandtl-number product. The function is shown graphically in Fig. 9-2. The ratio of apparent to true conductivity at values of the $N_{Pr}N_{Gr}$ product below 10,000 was independent of whether the gas layer was vertical or horizontal or of annular shape and of the direction of the temperature gradient. Nearly all the data were obtained at

⁵ W. H. McAdams, "Heat Transmission," 3d ed., p. 252, McGraw-Hill Book Company, Inc., New York, 1954.

⁶ H. Kraussold, *Forsch. Gebiete Ingenieurw.*, **5B**:186 (1934).

atmospheric pressure, and for application of Kraussold's relation at high pressures experimental confirmation was required. The value of D in the Grashof number is the width of the gas layer. Schmidt and Milverton⁷ studied heat transfer through various thicknesses of water and concluded that, if the product of Grashof and Prandtl numbers was less than 1,709, convection was absent.

As a means of testing for convection in the test gas layer used in the cylindrical thermal-conductivity cell used by Lenoir and Comings and described in Chap. 7, values of the Grashof and Prandtl numbers were computed, taking into account the non-perfect-gas behavior at high pressure. For the gases which were relatively close to the critical state,

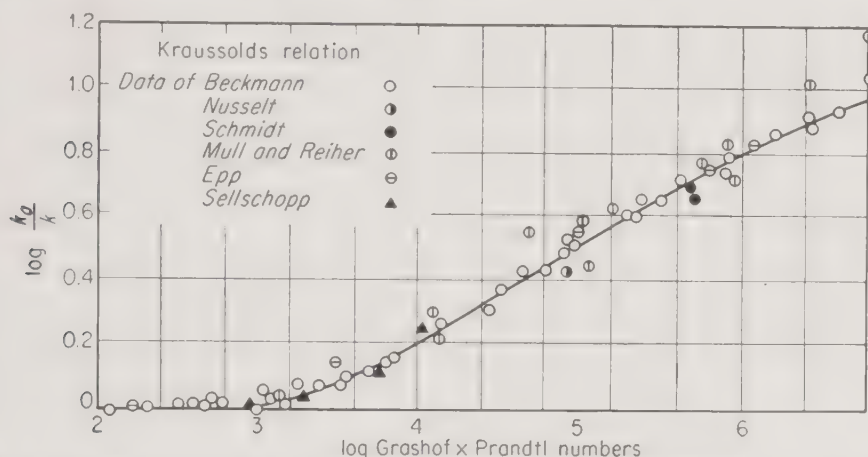


FIG. 9-2. Kraussold correlation of ratio of apparent to true thermal conductivity for heat transfer across a layer of fluid. [From J. M. Lenoir and E. W. Comings, *Chem. Eng. Progr.*, **47**:223 (1951).]

the value of $N_{Gr}N_{Pr}$ was found to reach a maximum at a pressure somewhat above the critical pressure. The sharpness of the maximum was more marked the closer the critical temperature was approached. This is illustrated for the case of carbon dioxide which approached closely to the conditions of incipient convection, and it was evident that an attempt to approach closer to the critical temperature would have resulted in convection. Nitrogen, on the other hand, does not approach the critical under the conditions chosen and is well below the convection zone. The variation of the $N_{Gr}N_{Pr}$ product with pressure for carbon dioxide and for nitrogen is shown in Fig. 9-3. In no case was a value of $N_{Gr}N_{Pr}$ found to be higher than 600.

A test was made in the thermal-conductivity cell under conditions of incipient convection as predicted by the high value in Fig. 9-3. At 106°F and 105 atm, measurements were made on carbon dioxide at tem-

⁷ R. J. Schmidt and S. W. Milverton, *Proc. Roy. Soc. (London)*, **152A**:586 (1935).

perature differences ranging from one-third to twice the normal temperature difference used in the cell. The apparent thermal conductivity is shown as a function of this ΔT in Fig. 9-4. The onset of convection is marked by the increase in apparent thermal conductivity. Below a

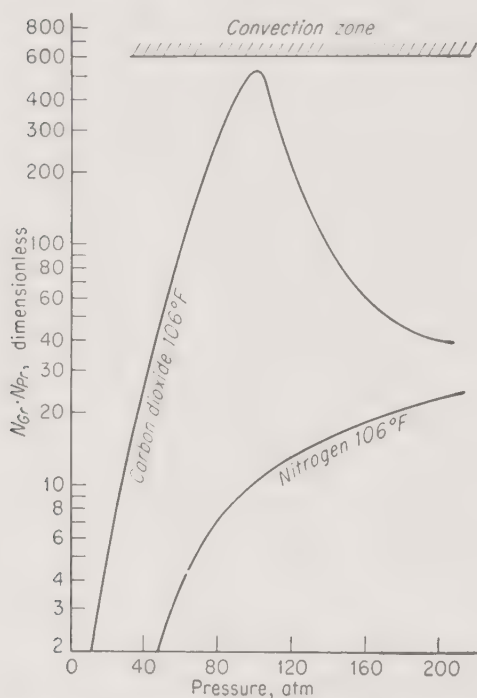


FIG. 9-3. Tendency of carbon dioxide and nitrogen to undergo convection as measured by Grashof- and Prandtl-number product. [From J. M. Lenoir and E. W. Comings, *Chem. Eng. Progr.*, **47**:223 (1951).]

Kraussold and suggests that his criterion for identifying the conditions which lead to natural convection may be applied at high pressure.

Boiling. When a volatile liquid is in contact with a surface and the temperature of the surface is higher than that of the liquid, heat is transferred from the surface to the liquid. If the temperature difference between the surface and the liquid is large enough, the liquid will boil provided other conditions are met. Cichelli and Bonilla⁸ have measured the rates of heat transfer and the temperature differences between a horizontal surface and a number of pure liquids and liquid mixtures during boiling. Two types of boiling were observed. *Nucleate boiling* is the type which is commonly observed, where bubbles form on the hot surface, break away, and rise through the hot liquid. As the temperature difference increases, the rate of heat transfer and also the violence of the boiling

critical value of $N_{Gr}N_{Pr}$ of 760, the measured value of thermal conductivity was found to be independent of temperature difference. Above 760, the value of the apparent thermal conductivity increased with increasing temperature difference. This test confirms the conclusions of

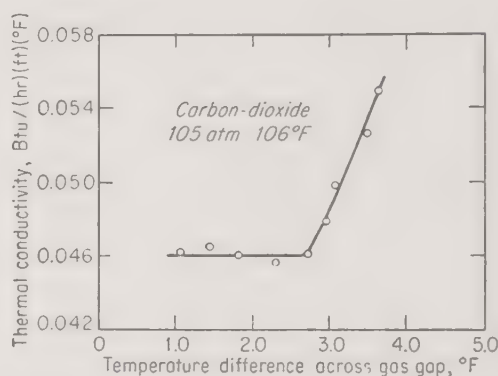


FIG. 9-4. Apparent thermal conductivity as measured increases abruptly when convection sets in. [From J. M. Lenoir and E. W. Comings, *Chem. Eng. Progr.*, **47**:223 (1951).]

⁸ M. T. Cichelli and C. F. Bonilla, *Trans. Am. Inst. Chem. Engrs.*, **41**:755 (1945).

increase. There is a well-defined limit to the increase in the rate of heat transfer. This occurs when the surface becomes covered with a continuous film of vapor, which then insulates the liquid from the hot surface, and the rate of heat transfer rapidly becomes much less. The boiling after the film formation is called *film boiling*. The rate of heat transfer at a given pressure is a maximum for nucleate boiling at the critical temperature difference ΔT_c just before the onset of film boiling. The values of ΔT_c (do not confuse this with the critical temperature which is

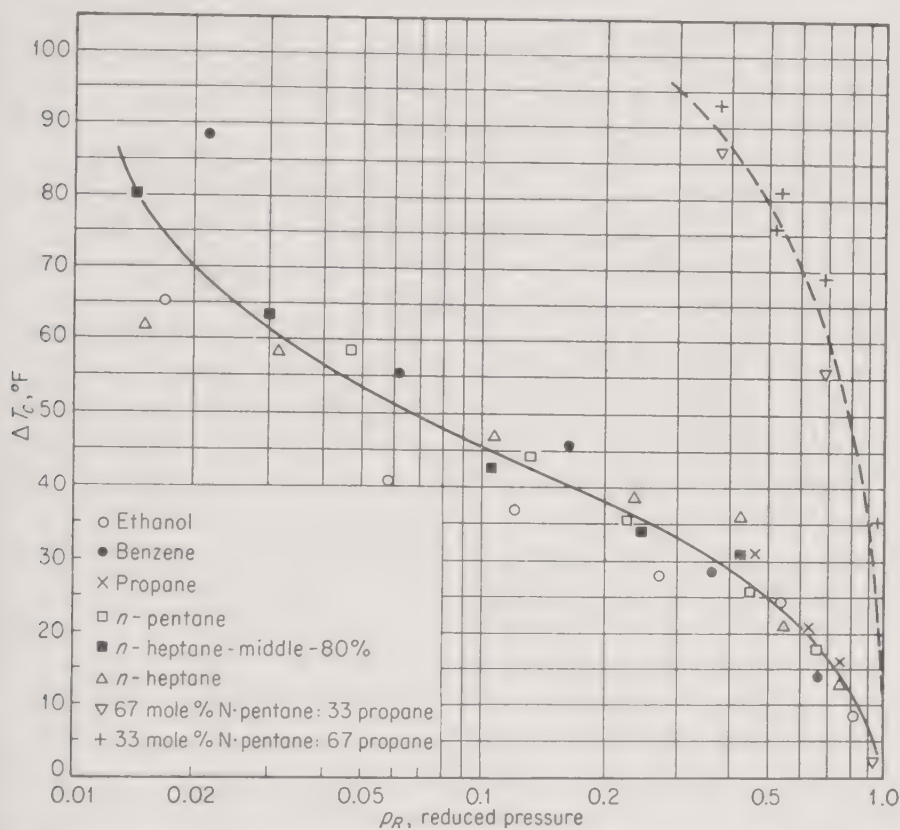


FIG. 9-5. Temperature differences at maximum boiling rate. [From M. T. Cichelli and C. F. Bonilla, *Trans. AICHE*, **41**:755 (1945).]

T_c) for pure compounds and for binary mixtures are correlated as a function of reduced pressure p_R in Fig. 9-5. Considerably higher values of ΔT_c are observed for binary mixtures than for pure compounds. The maximum rate of heat transfer extrapolates to zero as the pressure approaches zero and again as the pressure approaches the critical pressure p_c for the compound or mixture. Cichelli and Bonilla show that the maximum rate of heat transfer for nucleate boiling from a clean surface divided by the critical pressure is a function of the reduced pressure for the compounds and mixtures tested. This function is shown graphically

in Fig. 9-6. When the surface has become dirty, the heat-transfer rate is somewhat higher, probably because of the presence of more boiling nuclei. The measurements with dirty tubes may be brought into approximate agreement with those with clean tubes by dividing the maximum rate of the former by 1.15.

Straub⁹ has observed visually the boiling of water at pressures approaching the critical pressure. The density of the vapor in the bubbles approaches that of the liquid. The buoyant force on the bubbles is small and they rise through the liquid in a sluggish manner which does not resemble boiling at atmospheric pressure.

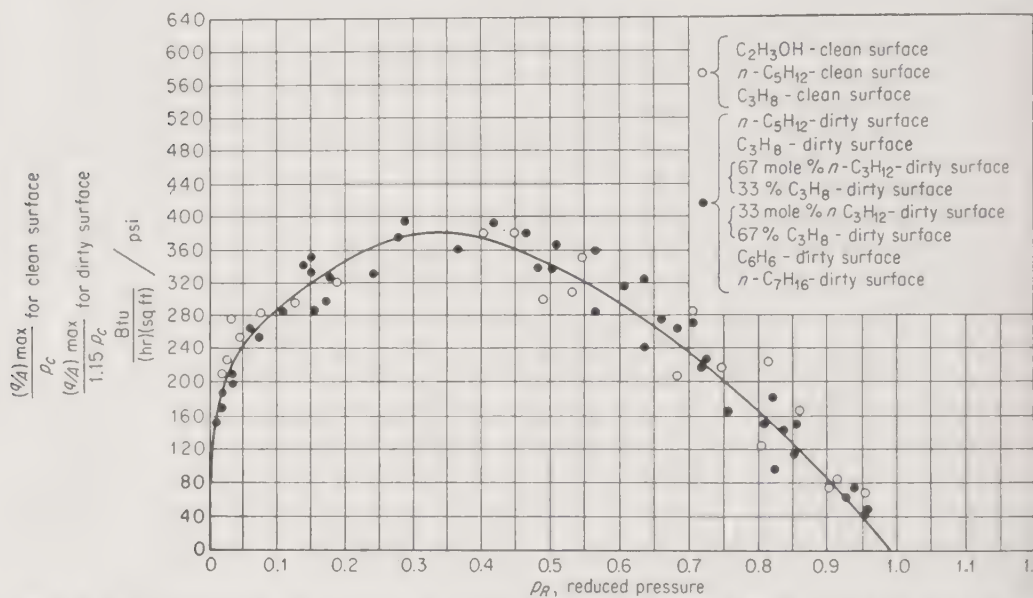


FIG. 9-6. Correlation of maximum boiling rates. [From M. T. Cichelli and C. F. Bonilla, *Trans. AIChE*, **41**:755 (1945).]

The critical pressure of certain mixtures was shown in Chap. 8 to be as high as a few hundred atmospheres. For such mixtures, boiling is possible at a higher pressure than for pure liquids. At pressures above the critical pressure, there is no longer a phase change from liquid to vapor and boiling does not occur.

9-2. Flow of Fluids. The flow of nonviscous fluids at high pressures through cylindrical tubes can be predicted for engineering purposes by the same methods used at low pressures. Such methods are adequately described in a number of other books¹⁰ and include the use of a Fanning friction factor correlated as an empirical function of the Reynolds number. This method of calculating the pressure drop associated with a given rate

⁹ F. G. Straub and H. A. Grabowski, *Trans. ASME*, **67**:309 (1945).

¹⁰ For example J. H. Perry, editor, "Chemical Engineers' Handbook," 3d ed., p. 381, McGraw-Hill Book Company, Inc., New York, 1950.

of flow along a tube is applicable to the flow of liquids and also of gases when the pressure drop per unit length is a moderate value.

Newitt and Sirkar¹¹ have carefully measured the resistance to flow through $\frac{1}{8}$ -in.- and $\frac{1}{32}$ -in.-nominal-diameter tubes using air, carbon dioxide, argon, nitrogen, hydrogen, and mixtures of hydrogen and nitrogen under pressure extending in the case of air up to 200 atm.. Considerable variation in the behavior of the friction factor was observed, but this was no greater than could be accounted for by tube roughness. Regions of streamline flow, critical flow, and turbulent flow were noted. The results in general confirm the validity of the method used at low pressure for flow under high-pressure conditions, although it is only approximate in many cases. The measurements were made with a carefully designed differential-pressure device and permitted the use of small pressure differences across the 12-ft length of tube. The empirical nature of this correlation should be clearly recognized. At times the friction factor has been incorporated into a mechanical energy balance. The resulting equation, which contains the term $V dp$, has been integrated, employing the friction factor, in much the same way that a reversible thermodynamic process is treated. While this procedure has been convenient in many cases, it lacks sound justification, since the presence of the friction term identifies the process as thermodynamically irreversible. It follows that the integration just described is not a valid procedure. This may not lead to serious errors at low pressures or with small pressure drops. With the large pressure drops possible in high-pressure operations, the method should be used with caution.

Large pressure drops associated with flow at high pressure may be accompanied by evaporation or flashing of a liquid. The behavior of the liquid under pressure should be investigated if phase-equilibrium information is not available. It is less likely to be available when the liquid is a mixture.

The handling of liquids under high pressure sometimes presents special problems. The temperature at which many liquids solidify is known to be higher at high pressure. Norton, Knott, and Muenger¹² have measured the behavior of lard, rapeseed oil, sperm oil, and Veedol medium (SAE 30) petroleum oil when flowing through a capillary tube at pressures up to 50,000 psi. The sperm and rapeseed oils showed definite solidification under pressure. All four oils behaved as non-Newtonian fluids displaying marked changes in "apparent" viscosity with pressure and with the rate of shear.

The design of valves to control the flow of fluids under high pressure and equipment to measure rates of flow are described in Chap. 5.

¹¹ D. M. Newitt and S. K. Sirkar, *Trans. Inst. Chem. Engrs. (London)*, **9**:63 (1931).✓

¹² A. E. Norton, M. J. Knott, and J. R. Muenger, *Trans. ASME*, **63**:631, 637 (1941).

9-3. Mass Transfer. Distillation, absorption, and extraction operations are at times carried out at relatively high pressures. In most instances, the same type of information and the same methods used for the design of apparatus for moderate pressure may be used for high pressure. Only a few investigations have contributed quantitative information of general utility and of special interest at high pressures.

Distillation. The reader is referred to other sources¹³ for a discussion of distillation practices and design methods. Phase-equilibrium relations

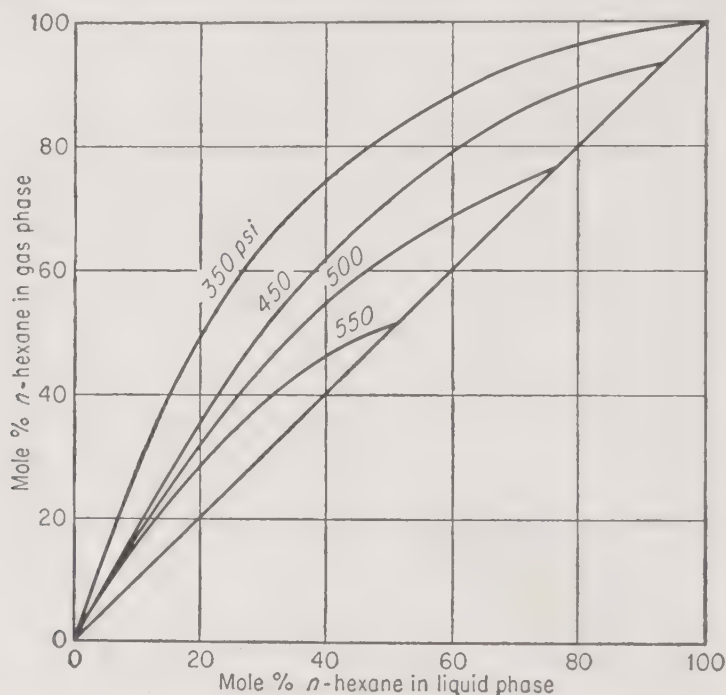


FIG. 9-7. Effect of pressure on xy phase equilibrium for toluene- n -hexane. [From L. M. Watson and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **48**(3):73 (1952).]

for two-component and multicomponent systems are of particular interest in the design of distillation columns. These relations have been considered in Chap. 8. An example of the effect of pressure on the xy equilibrium diagram for a two-component system is shown in Fig. 9-7. The system¹⁴ is toluene- n -hexane.

At higher pressures, the equilibrium curve for constant-pressure conditions approaches the curve for $x = y$. A larger number of distillation steps or trays is required for the same separation of the components under these conditions. This behavior is normal. Separation by distillation requires a larger number of steps at high pressures than at low. As the

¹³ C. S. Robinson and E. R. Gilliland, "Elements of Fractional Distillation," 4th ed., McGraw-Hill Book Company, Inc., New York, 1950.

¹⁴ L. M. Watson and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **48**(3):73 (1952).

critical pressure for the mixture is approached, there are ranges of composition where two phases do not coexist, and separation is not possible in these ranges. The curves for 450 psi and above behave in this fashion. If the number of trays were the main consideration, it would be desirable to carry out all distillations at low pressures. In some situations, this is actually more costly, and it is then more desirable to operate at elevated pressure.

Other factors sometimes favor operation at high pressures. The heat of evaporation, for instance, is lower as the critical condition is approached. The general temperature level of the tower is higher at high pressures. This permits the use of water at ambient temperature in the condensers and avoids the need for costly refrigeration. The viscosity of liquids flowing down the column will be lower, and this may be an advantage because of flow characteristics and contacting efficiency. The higher density of the vapor phase leads to a smaller column diameter for the same mass flow rate.

9-4. Absorption. Two phases have been reported under pressures approaching 10,000 atm with systems which separate into a liquid and gas at low pressures. It is thus possible to carry out a gas-absorption operation at high pressures. Some commercial gas-absorption units are now operated at several thousand pounds per square inch. The normal design of absorption equipment is adequately described in other texts¹⁵ and will not be covered here. Very few comprehensive investigations useful in designing high-pressure absorbers have been reported. Zabban and Dodge¹⁶ have determined the effect of the total pressure on the gas-film absorption coefficient in a packed tower over a range of pressures from 1 to 14 atm. The rate of mass transfer between the gas and liquid phases may be expressed by the equation

$$N_A \alpha dV = k_G \alpha p (y - y_i) dV$$

When the gas film comprises the major resistance, the concentration gradient in the liquid is small, and y_i at the interface is the same as the concentration y_L in the body of the liquid phase.

From the diffusion theory, the gas-film coefficient k_G is given by the expression

$$k_G = \frac{D_v p}{RT z p_{BM}} \quad (9-5)$$

According to Maxwell's definition,¹⁷ the molecular diffusivity D_r in this equation is equal to the group $R^2 T^2 / \alpha p$. By substituting this group for

¹⁵ T. K. Sherwood and R. L. Pigford, "Absorption and Extraction," 2d ed., McGraw-Hill Book Company, Inc., New York, 1952.

¹⁶ W. Zabban and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **50**(10):61 (1954).

¹⁷ J. C. Maxwell, *Cambridge Univ. Sci. Papers*, **2**:343 (1890).

D_r in Eq. (9-5), the relationship between k_G and p_{BM} obtained is

$$k_G = \frac{RT}{\alpha z p_{BM}} \quad (9-6)$$

The measurements by Zabban and Dodge are shown in Fig. 9-8 for the two systems air-methanol-water and air-acetone-water, the first in a

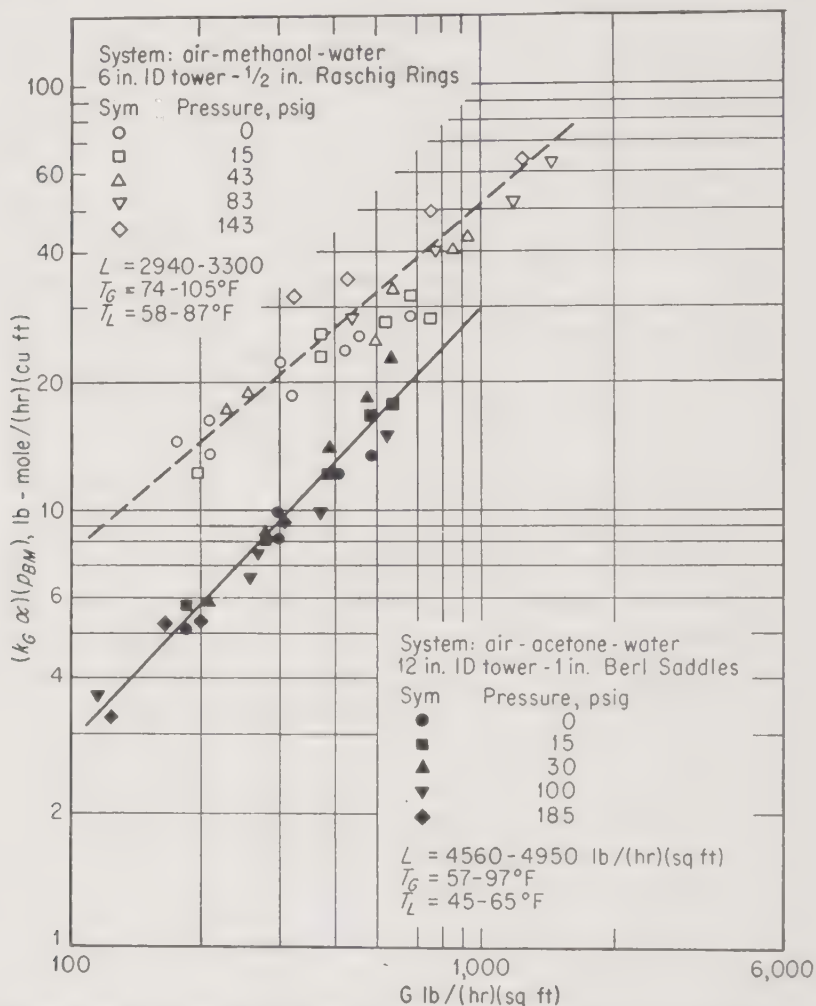


FIG. 9-8. Product of gas-film absorption coefficient and pressure vs. mass velocity of gas. [From W. Zabban and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser.*, **50**(10): 61 (1954).]

6-in.-ID tower packed with 1/2-in. Raschig rings and the second in a 12-in.-ID tower packed with 1-in. Berl saddles. The data from each system fall on single curves representing $k_G \alpha p_{BM}$ vs. G . Thus, the value of this product is the same at a fixed value of G regardless of the total pressure. This is to be anticipated from Eq. (9-6). These experiments demonstrate that the gas-film coefficient k_G is inversely proportional to

the mean partial pressure of the inert gas. This was roughly the same as the total pressure.

The effect of pressure on the molecular diffusivity D_v has been explored at relatively low pressures but not until recently under pressures approaching the critical pressure and higher. From the known behavior of viscosity and thermal conductivity (which are also transport properties), deviations from Maxwell's relation are to be expected in this region. The molecular diffusivity is discussed in Chap. 8.

No major changes in *liquid-liquid-extraction* apparatus should be expected at pressures up to a few hundred atmospheres. However, the design of gas pockets above a packed or spray column will be affected as will also the design of level and interface controllers and other auxiliary equipment.

NOMENCLATURE

a	Area of interphase contact, sq ft/cu ft
c_p	Specific heat, Btu/(lb)(°F)
D	Diameter, ft; width of gas layer
D_e	Equivalent diameter, equal to four times the hydraulic radius based on wetted perimeter, ft
D_v	Diffusivity for gas, sq ft/hr
f	Friction factor in Fanning equation, dimensionless; as subscript, indicates film conditions
G	Mass velocity of gas, lb/(hr)(sq ft)
g	Acceleration of gravity, ft/sec ²
h	Film coefficient for heat transfer, Btu/(hr)(sq ft)(°F); or Pec/(hr)(sq ft)(°C)
j	Factor equal to $h/c_p G \varphi$, dimensionless
k	Thermal conductivity, Btu/(hr)(ft)(°F); k_f , at film temperature
k_G	Gas-film diffusion coefficient, lb moles/(hr)(sq ft)(atm)
L	Length of tube, ft; mass velocity of liquid, lb/(hr)(sq ft)
N_A	Rate of diffusion, moles/(hr)(sq ft)
N_{Re}	$DU\rho/\mu$
N_{Fr}	$c_p\mu/k$
N_{Gr}	$(D^3\rho^2g/\mu^2)\beta\Delta t$
p	Total pressure, atm
p_R	Reduced pressure, p/p_c
p_c	Critical pressure, atm
p_{inert}	Logarithmic mean of partial pressure of inert gas at phase boundary and in bulk of gas
R	Gas-law constant, 0.728 (cu ft)(atm)/(lb mole)(°R)
T	Temperature, °R; T_G , of gas, °F; T_L , of liquid, °F
T_c	Critical temperature, °R
ΔT_c	Critical temperature difference for maximum rate of heat transfer in boiling

- U Average (bulk) velocity, ft/sec
- V Volume of absorption apparatus, cu ft; total volume of a fluid
- x Mole fraction of one component in liquid
- y Mole fraction of one component in gas
- y_i Mole fraction of solute in interface
- y_L Mole fraction in equilibrium with the bulk of the liquid
- z Effective thickness of gas film
- sub f Arithmetic average of values at phase boundary and in bulk of fluid
- α Ratio of surface area per volume of packing, sq ft/cu ft
- a Term in Maxwell's definition of diffusivity
- β Coefficient of thermal expansion $\frac{1}{V} \frac{dV}{dT}$; for a perfect gas, $\beta = 1/T$
- ρ Density, lb/cu ft
- φ Term in the definition of the "j" factor; for flow in tubes, $\varphi = (c_p \mu / k)_f^{1/2}$
- μ Viscosity, lb/(hr)(ft)

CHAPTER 10

CHEMICAL EQUILIBRIUM

It is important to distinguish between equilibrium and rate of reaction in a chemical reaction. Chemical-reaction equilibrium will be discussed in this chapter, and the rate of reaction in Chap. 11. The concept of chemical equilibrium is identical with that of thermodynamic reversibility applied to a system in which a chemical reaction may take place. When a reaction has progressed to equilibrium, it has reached the limiting extent to which the reaction can proceed under the prevailing set of conditions, such as temperature, pressure, composition, and the like. Thermodynamics is useful in predicting the conditions of chemical equilibrium. It will not, however, yield information concerning the mechanism or kinetics of the reaction or the rate of a reaction tending toward equilibrium as a limit. Changes in the operating conditions or the introduction of another reactant may alter considerably the state of equilibrium in a system. Thermodynamics will not automatically indicate that there is such an alteration which will favorably affect the reaction equilibrium. However, it may be applied to proposed changes and will then indicate which of these are likely to be advantageous.

The equilibrium composition may be determined for a particular point in a reactor in which conditions change from point to point or for a reactor as a whole when conditions are essentially uniform throughout. Thermodynamics tells us that equilibrium prevails when a small, or, more precisely, a differential, amount of reaction taking place under constant temperature and pressure results in a free-energy change of zero. This criterion may be used to relate the composition at equilibrium to the free-energy change for the reaction.

Thermodynamics may also be applied to the over-all reaction carried out reversibly starting with the reactants in a certain specified condition and ending with the products in another specified condition. When so applied it gives no information about the equilibrium composition but indicates the limiting amount of energy either required to operate the process or produced by the process. This information is of considerable importance in evaluating the commercial feasibility of a proposed process. The over-all reaction will be considered first, and then the composition at

equilibrium. The discussion will be limited to reactions involving gases only.

10-1. An Isolated System. The second law of thermodynamics leads to Clausius' statement¹ that the entropy of an isolated system must either remain constant or increase. It cannot decrease. This statement may be employed to determine the limiting amount of energy as work and heat which must be exchanged between the system and its surroundings when a given chemical reaction takes place. In order to apply this statement the reaction as well as its surroundings are made part of an isolated system. To do this, consider two systems α and β . All the reactants and products of the reaction will at all times be contained in system α . System β may receive heat and work from system α or contribute them to system α . The two systems α and β taken together constitute an isolated system, and neither matter nor energy may be exchanged between this system and the outside.

In general the reactants and products which make up part of system α may be at different pressures and temperatures. The energy \mathcal{E}_α and the entropy \mathcal{S}_α of the system α will be the sum of the energy and entropy of the various parts of the system α . Similarly \mathcal{E}_β and \mathcal{S}_β are the energy and entropy of the system β .

Since the two systems together are isolated,

$$\mathcal{E}_\alpha + \mathcal{E}_\beta = \text{constant} \quad (10-1)$$

and, according to Clausius' statement,

$$d\mathcal{S}_\alpha + d\mathcal{S}_\beta \geq 0 \quad (10-2)$$

The equality of Eq. (10-2) holds when all changes are reversible or at equilibrium. Since β serves only as a source of heat or work for α or an absorber of heat or work from α , all changes in β will arbitrarily be restricted to reversible changes. System β will have a constant temperature T_0 and a constant pressure p_0 . When heat is transferred to or from a region in system α at a temperature other than T_0 , it will be passed through a reversible heat engine and the maximum conversion to work obtained. Let Q_β represent heat added to β , and W represent work passing to β . Then since

$$d\mathcal{E}_\alpha = -\delta Q_\beta - \delta W \quad (10-3)$$

$$d\mathcal{S}_\beta = \frac{\delta Q_\beta}{T_0} = \frac{-d\mathcal{E}_\alpha - \delta W}{T_0} \quad (10-4)$$

Substituting Eq. (10-4) in Eq. (10-2),

$$d\mathcal{S}_\alpha - \frac{d\mathcal{E}_\alpha + \delta W}{T_0} \geq 0 \quad (10-5)$$

¹ B. F. Dodge, "Chemical Engineering Thermodynamics," pp. 80, 127, McGraw-Hill Book Company, Inc., New York, 1944.

An Idealized Reaction System. The Clausius statement and the relations derived from it apply to real systems and processes. In the limit, the entropy of an isolated system remains constant during changes in the system. This behavior is seldom attained in real systems but is nevertheless of interest because it represents reversible or equilibrium conditions.

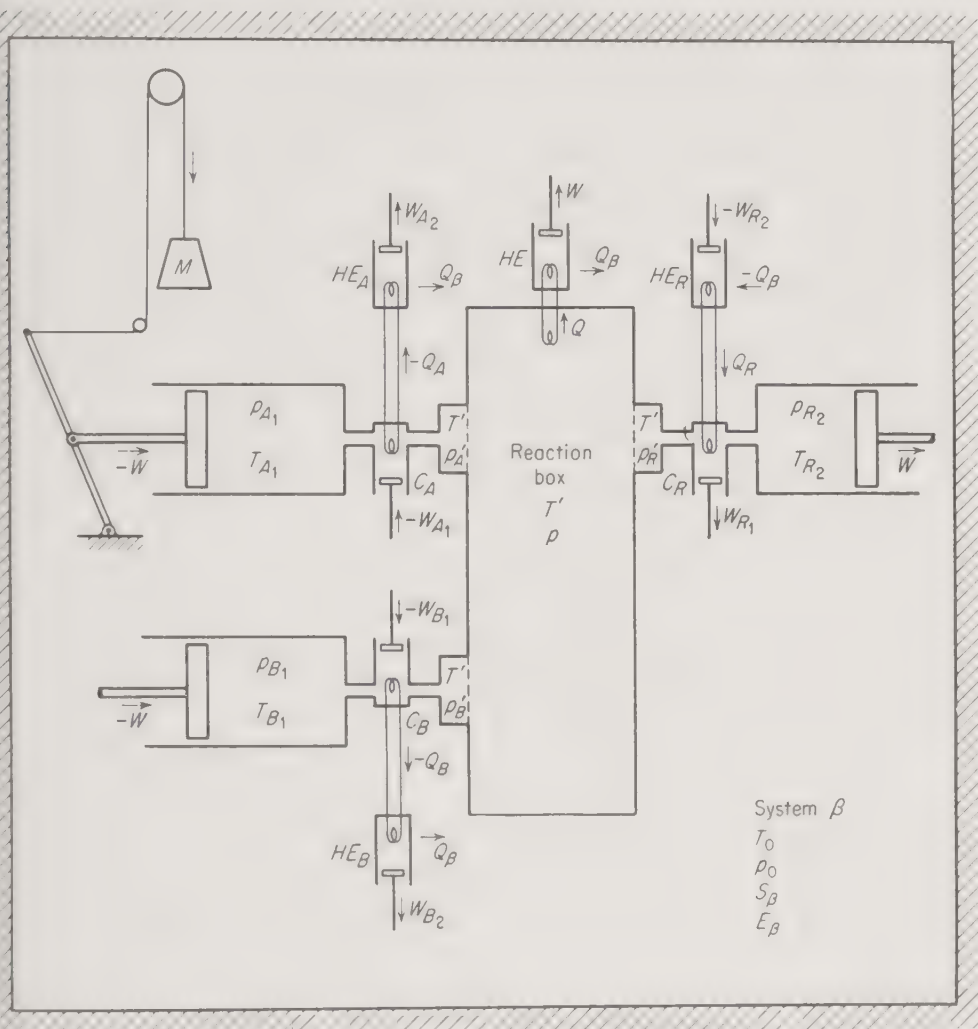
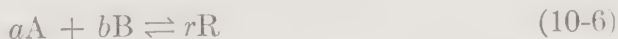


FIG. 10-1. Model of an isolated reaction system.

A hypothetical arrangement of systems α and β will be useful as a model for following the discussion of chemical processes. Such an idealized arrangement of systems α and β will now be devised to provide for a typical reaction,



which takes place in system α . This arrangement is shown in Fig. 10-1, representing an isolated system. The reactant A under a pressure p_{A1} is contained in a cylinder closed by a piston. Movement of the piston is

used to feed A to a compressor C_A and thence into a box where the reaction takes place under equilibrium concentrations. Reactant A is compressed in C_A to a pressure equal to the pressure of A, p'_A , in equilibrium with the reaction mixture in the box through a membrane permeable only to A and enters the box through the membrane. A similar arrangement is provided for reactant B, and also for the product R operating in reverse. The system β must provide work to move the piston feeding A and B to the compressors C_A and C_B and also to operate the compressors. A typical provision is shown in Fig. 10-1 as a mass M arranged to drive the piston for A. Similar arrangements may be visualized for the other pistons. Work done by the product-expansion engine C_R and the piston closing the product cylinder will be added to system β . The work done on the reactant and product cylinders is at a constant pressure and will be considered separately from that done on the compressors. The work done on the compressors and the reversible heat engines by system β will be designated $-\Sigma W'$. The compressors C_A and C_B and expander C_R are small compared to the reactant and product cylinders and contain only a differential quantity of material at any instant. Then, for a small addition of reactants to the box and a small removal of product,

$$-S_A da - S_B db + S_R dr + dS_\beta \geq 0 \quad (10-7)$$

$$\text{and} \quad -\delta Q_\beta = dE_\alpha + \Sigma \delta W \quad (10-8)$$

where $\Sigma \delta W$ is all the work done on β either by the compressors or expanders or by the reactant and product cylinders, or by the reversible heat engines HE_A , HE_B , etc. For a differential reaction

$$dE_\alpha = -E_{A_1} da - E_{B_1} db + E_{R_2} dr \quad (10-9)$$

and from Eqs. (10-4), (10-7), and (10-9)

$$-S_{A_1} da - S_{B_1} db + S_{R_2} dr + \frac{E_{A_1} da}{T_0} + \frac{E_{B_1} db}{T_0} - \frac{E_{R_2} dr}{T_0} - \frac{\Sigma \delta W}{T_0} \geq 0 \quad (10-10)$$

$$\text{or} \quad -(E_{A_1} - T_0 S_{A_1}) da - (E_{B_1} - T_0 S_{B_1}) db + (E_{R_2} - T_0 S_{R_2}) dr \leq -\Sigma \delta W \quad (10-11)$$

Equation (10-11) indicates that the total work $-\Sigma \delta W$ done on the system α by the system β is at least equal to the sum of the change in $E - T_0 S$ for all the components consumed and products formed by the reaction. There is no restriction on the temperature or pressure of the reactants or products, but system β is at a uniform temperature T_0 . If the reactants and products are also at T_0 , then the subscript 0 may be dropped and the work done must be at least ΔA , where A is $E - TS$, called the work function. The reactants, products, and system β are then at the constant temperature T .

pV Work Considered Separately. The total work $-\Sigma\delta W$ may be divided into the work $p_{A_1}v_{A_1} da$, $p_{B_1}v_{B_1} db$, etc., done on the reactants in forcing them out of their original cylinders and the work done by the products in entering their cylinders at their respective pressures, as one part; the work other than this is the other part, previously designated $-\Sigma\delta W'$. Then for a and b moles reacting to form r moles of products,

$$-(E_{A_1} - T_0 S_{A_1} + p_{A_1} v_{A_1})a - (E_{B_1} - T_0 S_{B_1} + p_{B_1} v_{B_1})b \\ + (E_{R_2} - T_0 S_{R_2} + p_{R_2} v_{R_2})r \leq -\Sigma W' \quad (10-12)$$

When the temperature of reactants and products is T_0 , Eq. (10-12) may be written

$$(E_{R_2} - T_{R_2} S_{R_2} + p_{R_2} v_{R_2})r - (E_{A_1} - T_{A_1} S_{A_1} + p_{A_1} v_{A_1})a \\ - (E_{B_1} - T_{B_1} S_{B_1} + p_{B_1} v_{B_1})b \leq -\Sigma W' \quad (10-13)$$

provided that $T_{R_2} = T_{A_1} = T_{B_1} = T_0$. The terms in parenthesis are the free energies, by definition, and

$$rF_{R_2} - aF_{A_1} - bF_{B_1} \leq -\Sigma W' \quad (10-14)$$

This may be written

$$\Delta F \leq -\Sigma W' \quad (10-15)$$

and the equality applies when the process takes place reversibly. When the reaction in the box takes place at equilibrium and the pistons and compressors operate reversibly, the process is reversible: the work $\Sigma W'$ is the work of a reversible process and may be designated $\Sigma W'_R$, and

$$\Delta F = -\Sigma W'_R \quad (10-16)$$

This equation applies when the reactants are initially at the temperature of the surroundings and the products are brought to this temperature. There is no restriction that the reaction take place at this same temperature, and Eq. (10-16) applies when the reaction takes place at any temperature provided all changes are reversible.

The total work $-\Sigma\delta W$ may also be divided into two other parts. The first part is the sum of $p_0 v_{A_1} da$, $p_0 v_{B_1} db$, etc., which is the work done by the surroundings (system β) at the pressure of the surroundings p_0 in forcing the reactants out of their cylinders and by the products on the surroundings in entering their cylinders. The second part consists of the remainder of the work and is designated $-\Sigma\delta W''$. If the reactants and products are not at the pressure p_0 , work in addition to that considered in the first part (that is, $p v - p_0 v$) will be required in forcing them out of their cylinders. This is included in $-\Sigma\delta W''$. Then

$$-(E_{A_1} - T_0 S_{A_1} + p_0 v_{A_1})a - (E_{B_1} - T_0 S_{B_1} + p_0 v_{B_1})b \\ + (E_{R_2} - T_0 S_{R_2} + p_0 v_{R_2})r \leq -\Sigma W'' \quad (10-17)$$

The equality applies when the reaction is carried out reversibly and the pistons and compressors operate reversibly. Under these conditions, Eq. (10-17) indicates the maximum amount of work, other than that done by expansion at the pressure p_0 , which may be obtained from the reaction, or, conversely, the minimum work which must be performed if the reaction is to take place. Equation (10-17) is general, since the reactants and products may be at any specified temperatures and pressures. Equation (10-17) also reduces to Eq. (10-15) provided the temperatures and pressures are all the same and are equal to T_0 and p_0 . These equations provide the basis for determining the limiting amount of energy required as work for a chemical reaction.

10-2. Energy Requirements for a Chemical Reaction. The energy requirements for a chemical reaction carried out reversibly are completely fixed by the initial state of the reactants and the final state of the products. Energy may be supplied to the reaction or obtained from it, as the case may be, as heat, as p_0v work at the pressure of the surroundings, and as work energy transferred to the reaction by other means and designated as $-\Sigma W''$. The sum of the heat and work are the energy requirements ΔE for the reaction as obtained by integrating Eq. (10-9), while the portion which must be supplied as work $-\Sigma W''$ is given by Eq. (10-17). If the reaction is capable of doing work, this equation indicates the maximum amount of such work. This work is obtainable if the reaction is carried out reversibly. If the reaction requires that work be done on it, the equation indicates the minimum amount of such work, again under reversible conditions. More of the total energy requirement may be supplied as work, but the reaction is then not reversible. If the reaction can take place without the expenditure of work on it, it is said to be spontaneous.

If the initial and final pressures and temperatures of the reactants and products are those of the surroundings, then $\Sigma W''$ is the same as $\Sigma W'$, the limiting value of which is $-\Delta F$. In any case, the limiting value of $\Sigma W'$ is $-\Delta F$, as shown by Eq. (10-16). Thus, values of ΔF for the reaction indicate the amount of work to be done on the reaction under ideal (reversible) conditions when reactants and products are at the temperature of the surroundings.

The Standard State. In comparing reactions and tabulating free-energy data, a uniform set of conditions at any temperature is usually chosen for each substance, and when under these conditions the substance is said to be in its standard state. For gas-phase or heterogeneous gaseous chemical reactions, it will be convenient to use the fugacity as discussed later. The standard states of the pure gaseous reactants and products at any temperature will be taken as the states in which the individual fugacities are unity. For perfect gases this is identical with choosing the standard state at 1 atm and for nonperfect gases the pressure at unit fugacity will

not differ greatly from 1 atm. If the pressures specified for reactants and products are those for the standard states of these compounds, the free-energy change is known as the standard free-energy change and is represented by ΔF° .

$$\Delta F^\circ = -\Sigma W_R'^\circ \quad (10-18)$$

$-\Sigma W_R'^\circ$ is the additional work in excess of that furnished at the pressure of the surroundings to convert the pure reactants in their standard states to pure products in their standard states by a reversible process.

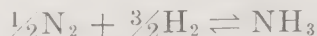
Free-energy Change at Equilibrium. When the initial pressures of the reactants and the final pressure of the products are the pressures exerted through the semipermeable membranes by the mixture at equilibrium within the box, then no additional work other than that required to feed the reactants and remove the products is required and $\Delta F = 0$.

It is evident that if one starts with reactants at a given temperature and pressure and wishes to make a product at a given temperature and pressure, neither the total energy nor the minimum work required by the process can be altered by carrying out the reaction at either higher or lower pressures. However, in practice the work done on the process may greatly exceed the minimum requirements, and much additional heat may be discarded. For example, in the synthetic-ammonia process the ideal energy requirements are the same when the reaction is carried out at 1 atm as when the reactants, initially at 1 atm, are compressed to 300 atm, the reaction carried out at this pressure, and the resulting ammonia recovered and delivered at 1 atm. However, when the process is actually operated at 1 atm, only a very small percentage of ammonia is formed at equilibrium, and the low efficiencies encountered in recovering this weak ammonia, concentrating and compressing it to 1 atm, and recycling the unconverted reactants result in actual energy expenditures greatly in excess of the minimum requirements. Operation under pressure then results in a very great increase in efficiency. This illustration indicates the importance of the effect of pressure on the composition of the reaction mixture at equilibrium. Thermodynamics may be used to predict the composition when equilibrium is reached at various pressures. Before describing how this is done, let us consider further the over-all energy requirements and their relation to the feasibility of a reaction.

Commercial Feasibility of a Chemical Reaction. The commercial feasibility of a chemical reaction is largely a question of economics. When energy must be supplied to a reaction, the value of the energy must be charged as part of the cost of operating the process. Energy supplied as work is more costly than that supplied as heat, and thus higher values of ΔF° for a reaction indicate that its commercial operation is less likely to be feasible unless there is a correspondingly greater increase in the value

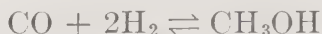
of the products as compared to the reactants. A few examples will clarify this statement.

At 700°K, the reaction



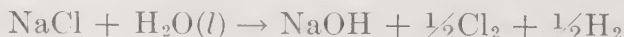
has a ΔF° of +6540 cal/mole, and this energy must be supplied as work. The reaction takes place to a negligible extent at 1 atm, but it attains commercial importance when operated at a few hundred atmospheres pressure. The work is supplied in the gas compressors, and the value of the ammonia compared with that of hydrogen and nitrogen is enough to pay for the processing.

The reaction



at 648°K has a ΔF° of +12,400 cal/mole, which might place it on the doubtful list because of the cost of supplying this much energy as work. It is operated commercially at several hundred atmospheres pressure. This is another illustration of a case where the handicap of a high ΔF° has been overcome, and the reaction is in commercial operation.

As another illustration, the reaction



has a large positive ΔF° of +57,920 cal/mole at 298°K. This would seem to indicate that the reaction could not be carried out commercially. By carrying it out in an electrolytic cell and introducing electric energy at least equivalent to ΔF° , the reaction takes place readily. The caustic and chlorine are considerably more valuable than salt, and the process is commercially profitable.

The possibility of making modifications in an otherwise unfavorable reaction should not be overlooked. In this respect, the reaction



has a ΔF° at 500°K of +49,600 kcal/mole, and thus the prospect of forming longer-chain hydrocarbons from methane seems poor. Recalling that oxygen reacts with methane with a large negative ΔF° , it is evident that if enough oxygen is added to react with one of the hydrocarbons this places the above reaction in a much more favorable position from the thermodynamic point of view. The reaction



at 500°K has a ΔF° of -7,100 and offers considerable promise. This is the sort of modification applied in the Fischer-Tropsch process, which

employs a higher temperature, and represents the use of a negative ΔF for one reaction to balance the positive ΔF of another. The work or high-level-energy requirements of the first reaction are supplied by the free energy of another chemical reaction.

The handicap of a high positive ΔF° is not entirely due to the cost of supplying the energy. This energy cannot be supplied as heat, and thus a way must be found to introduce work or electric energy directly to the reaction. The engineering problems involved in doing this are usually more complicated than when energy can be added as heat, and these complications place a limit on the amount of energy which can be supplied economically in the form of work.

10-3. Composition at Reaction Equilibrium. The effect of pressure on the composition of the reaction mixture at equilibrium will now be considered. The typical reaction shown by Eq. (10-6) will be carried out reversibly with equilibrium being attained in the reaction box. The change of free energy accompanying this reaction is shown by Eq. (10-16).

$$\Delta F = -\Sigma W'_R \quad (10-16)$$

The work $-\Sigma W'_R$ may be added to the system α in several ways. It may be introduced in an equilibrium cell as electric energy. If the reaction is at an elevated pressure, it may be the difference between the work of compression of the reactants and the work of expansion of the products. The shaft work delivered to or recovered from the compressors which deliver reactants to the reaction box or expand the products from the box will be calculated. If the pure reactants and product are in equilibrium with the mixture of gases within the box through their separate semi-permeable membranes at the pressures p'_A , p'_B , and p'_R , respectively, then for $T_A = T_B = T_R = T_0$

$$-\Delta F = \Sigma W'_R = r \int_{p_{R'}}^{p_{R2}} v_R dp_R - a \int_{p_{A'}}^{p_{A1}} v_A dp_A - b \int_{p_{B'}}^{p_{B1}} v_B dp_B \quad (10-19)$$

For an isothermal process, the integrations on the right may be carried out and conveniently expressed in terms of the fugacity f . Referring to Eq. (8-55),

$$v_A dp_A = RT d \ln f_A \quad (8-55)$$

Then at constant temperature

$$- \int_{p_{A1'}}^{p_{A1}} v_A dp_A = -RT \ln \frac{f_{A1}}{\bar{f}_A} = RT \ln \frac{\bar{f}_A}{f_{A1}} \quad (10-20)$$

and, by substituting the equivalent expression for each component in Eq. (10-19),

$$\begin{aligned}
 -\Delta F = \Sigma W'_R &= -RT \left(r \ln \frac{\tilde{f}_{R_2}}{\tilde{f}_R} + a \ln \frac{\tilde{f}_A}{\tilde{f}_{A_1}} + b \ln \frac{\tilde{f}_B}{\tilde{f}_{B_1}} \right) \\
 &= RT \left(-\ln \frac{\tilde{f}_{R_2}^r}{\tilde{f}_{A_1}^a \tilde{f}_{B_1}^b} + \ln \frac{\tilde{f}_R^r}{\tilde{f}_A^a \tilde{f}_B^b} \right) \quad (10-21)
 \end{aligned}$$

When the reactants and products are in their standard states their fugacities $\tilde{f}_{A_1}^\circ$, $\tilde{f}_{B_1}^\circ$, and $\tilde{f}_{R_2}^\circ$ are each unity and Eq. (10-21) reduces to

$$-\Delta F^\circ = \Sigma W'_R{}^\circ = RT \ln \frac{\tilde{f}_R^r}{\tilde{f}_A^a \tilde{f}_B^b} = RT \ln K \quad (10-22)$$

where K is the equilibrium constant at the temperature for which ΔF° is evaluated.

Predicting the Equilibrium Composition. The discussion to this point has been rigorous and involves no assumptions other than the validity of the second law of thermodynamics, which we will fully accept. Thus, the equilibrium constant

$$K = \frac{\tilde{f}_R^r}{\tilde{f}_A^a \tilde{f}_B^b} \quad (10-23)$$

depends only on the temperature and on the standard states chosen for the reactants and products and is independent of the pressure at which the reaction occurs (in the reaction box).

If the process is carried out reversibly at constant temperature starting with reactants in their standard states and ending with products in their standard states, the free-energy change for the process is independent of the pressure existing in the reaction box. The free-energy change is also independent of the temperature in the reaction box. In order to employ the free-energy concept, it is required that $T_{A_1} = T_{B_1} = T_{R_2} = T_0$. If fugacities are used, as in Eq. (10-22), the whole process must be isothermal. The equilibrium constant K as defined above is independent of the pressure in the box. When the process is isothermal the pressures p'_A , p'_B , and p'_R would in all cases be such that the corresponding fugacities are related so as to give a constant value of K at all total pressures. But since the fugacities change with pressure, the composition in the box at equilibrium also changes with pressure. Each of the fugacities could be evaluated from a knowledge of the relation between pressure and volume for pure A, B, and R over the range from the pressure at the standard state to p'_A , p'_B , and p'_R , respectively, according to Eq. (10-20).

In any actual reactor, the product will be removed not as a pure compound but in a mixture with other products, reactants, and inert components. In order to predict the composition of the product, it is important to determine the effect of pressure on the composition of the equilibrium mixture. This effect could be predicted if complete pVT -composition data were available for the mixtures concerned. Almost

without exception, such data for mixtures are not available, and predictions must be based on simplifying assumptions in lieu of the actual data. In many cases, relatively accurate predictions of the effect of pressure on equilibrium composition can be made within the limitations of the simplifying assumptions.

In relating the composition at equilibrium to the pressure at which the reaction occurs, it will be convenient to use the fugacity coefficient $\bar{\phi}_A$. The fugacity coefficient has been defined as follows^{2,3}

$$\bar{\phi}_A = \frac{\bar{f}_A}{y_A p}$$

or

$$\bar{f}_A = \bar{\phi}_A p y_A \quad (8-125)$$

Substituting Eq. (8-125) in Eq. (10-23)

$$K = \frac{\bar{\phi}_R^r}{\bar{\phi}_A^a \bar{\phi}_B^b} \frac{y_R^r}{y_A^a y_B^b} p^{r-a-b} \quad (10-24)$$

The ratio of the fugacity coefficients is denoted by K_ϕ , where

$$K_\phi = \frac{\bar{\phi}_R^r}{\bar{\phi}_A^a \bar{\phi}_B^b} \quad (10-25)$$

Equation (10-24) may be written

$$K = K_\phi \frac{y_R^r}{y_A^a y_B^b} p^{r-a-b} \quad (10-26)$$

At any constant temperature, K is a constant independent of pressure and of the composition of the equilibrium mixture, but K_ϕ will vary with the total pressure, with the temperature, and with the composition of the mixture. Equation (10-26) applies rigorously provided a rigorous method is used to evaluate K_ϕ . Ordinarily simplifying assumptions are made in the evaluation of K_ϕ , and the validity of the calculated results then depends on how well the simplifying assumption applies to the system being considered.

Equilibrium with Perfect Gases. A simple case is that involving only perfect gases, which always form ideal mixtures. The fugacities are then equal to the partial pressures of the individual components, and these are given by the product of the total pressure of the equilibrium mixture and mole fraction of each component. Thus,

$$f_A = p y_A \quad \text{and} \quad K = K_p = \frac{y_R^r}{y_A^a y_B^b} p^{r-a-b} \quad (10-27)$$

In this case, K_ϕ is unity.

² O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. II, Thermodynamics, p. 715, John Wiley & Sons, Inc., New York, 1947.

³ O. Redlich and J. N. S. Kwong, *Chem. Revs.*, **44**:233 (1949).

10-4. Ideal Mixtures. When the components of the gaseous mixture are not perfect gases but yet form an ideal mixture, Lewis and Randall⁴ have proposed the simplifying rule that the fugacity of any component in the mixture is the product of the fugacity of that pure component at the temperature and total pressure of the mixture and the mole fraction of the component in the mixture. Thus

$$\bar{f}_A = f_A y_A \quad (10-28)$$

This rule has been shown⁵ to apply when there is no volume change on mixing at all pressures up to the equilibrium pressure. It does not apply to nonideal mixtures. It indicates that K_ϕ may be calculated from the fugacity coefficients of the pure components determined at the temperature and total pressure of the equilibrium mixture. K_ϕ calculated in this manner is independent of the composition of the mixture. As K_ϕ approaches unity, Eq. (10-26) approaches Eq. (10-27) for a mixture of perfect gases. Equation (10-26), together with a knowledge of the equilibrium constant K and of the fugacity coefficients as a function of temperature and pressure for the several components, may be used to calculate the composition of the equilibrium mixture for ideal mixtures of gases. This is not limited to perfect gases, although most gases cease to form ideal mixtures when they cease to behave as perfect gases. The method just described is used in the following examples. The general effect of pressure on equilibrium composition is shown by the following problem.

Example 10-1. A mixture consisting of 2 moles of hydrogen and 1 mole of carbon monoxide reacts partially to form methanol. When this mixture has reached equilibrium, calculate its composition over a range of pressures from 100 to 500 atm at 250, 350, and 450°C and from 10 to 1,000 atm at 300°C. The equilibrium constants for the reaction $\text{CO}(g) + 2\text{H}_2(g) = \text{CH}_3\text{OH}(g)$ as calculated by Ewell⁶ are

°C	K	°C	K
100	10.84	350	4.458×10^{-5}
200	1.695×10^{-2}	400	1.091×10^{-5}
250	1.629×10^{-3}	450	3.265×10^{-6}
300	2.316×10^{-4}	500	1.134×10^{-6}

The values of K_ϕ as calculated by Newton and Dodge⁷ are shown in Fig. 10-2.

⁴ G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

⁵ S. Glasstone, "Thermodynamics for Chemists," pp. 267, 278, D. Van Nostrand Company, Inc., New York, 1947.

⁶ R. H. Ewell, *Ind. Eng. Chem.*, **32**:147 (1940).

⁷ R. H. Newton and B. F. Dodge, *Ind. Eng. Chem.*, **27**:577 (1935).

Solution. Basis: 1 mole CO + 2 moles H₂. Let x = moles CH₃OH formed at equilibrium. Then at equilibrium

$$\begin{aligned}\text{Moles CH}_3\text{OH} &= x \\ \text{Moles CO} &= 1 - x \\ \text{Moles H}_2 &= 2(1 - x) \\ \text{Total moles} &= 3 - 2x\end{aligned}$$

and substituting in Eq. (10-26)

$$K = \frac{K_\phi}{p^2} \frac{\frac{x}{3-2x}}{\frac{1-x}{3-2x} \left[\frac{2(1-x)}{3-2x} \right]^2} \quad \text{or} \quad \frac{Kp^2}{K_\phi} = \frac{x(\frac{3}{2} - x)^2}{(1-x)^3}$$

By substituting a number of values of x in the term on the right-hand side of this equation, several values of this term may be obtained. These values are

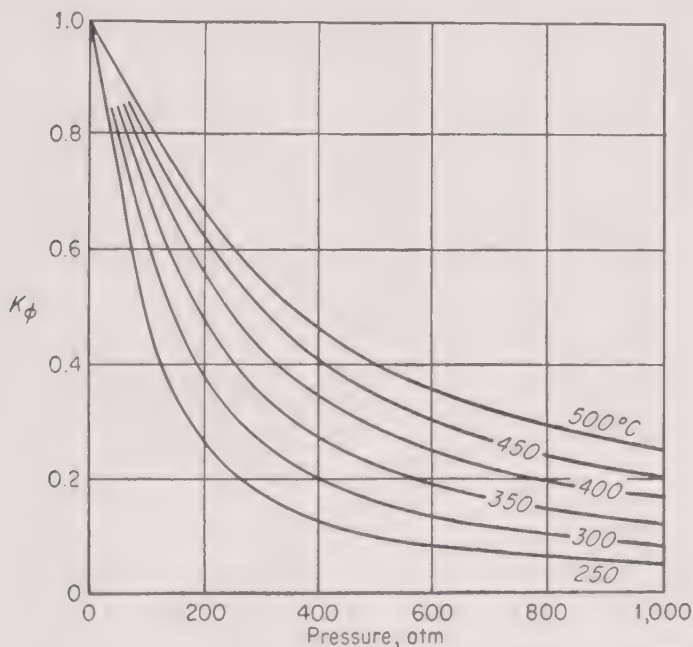


FIG. 10-2. Values of K_ϕ for the reaction $\text{CO}(g) + 2 [\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)]$. From R. H. Newton and B. F. Dodge. *Ind. Eng. Chem.*, **27**:577 (1935).]

shown graphically in Fig. 10-3. At a constant temperature, the term Kp^2/K_ϕ is a function of pressure. This relation is also shown on Fig. 10-3 at a temperature of 300°C. The value of x may be read directly from such a figure. Kp^2/K_ϕ is obtained at a given temperature and pressure, and the value of x is read from the point on the curve for the right-hand term corresponding to this value. The mole per cent of the components may then be calculated. The calculations are tabulated in Table 10-1, and the results are shown in Fig. 10-4.

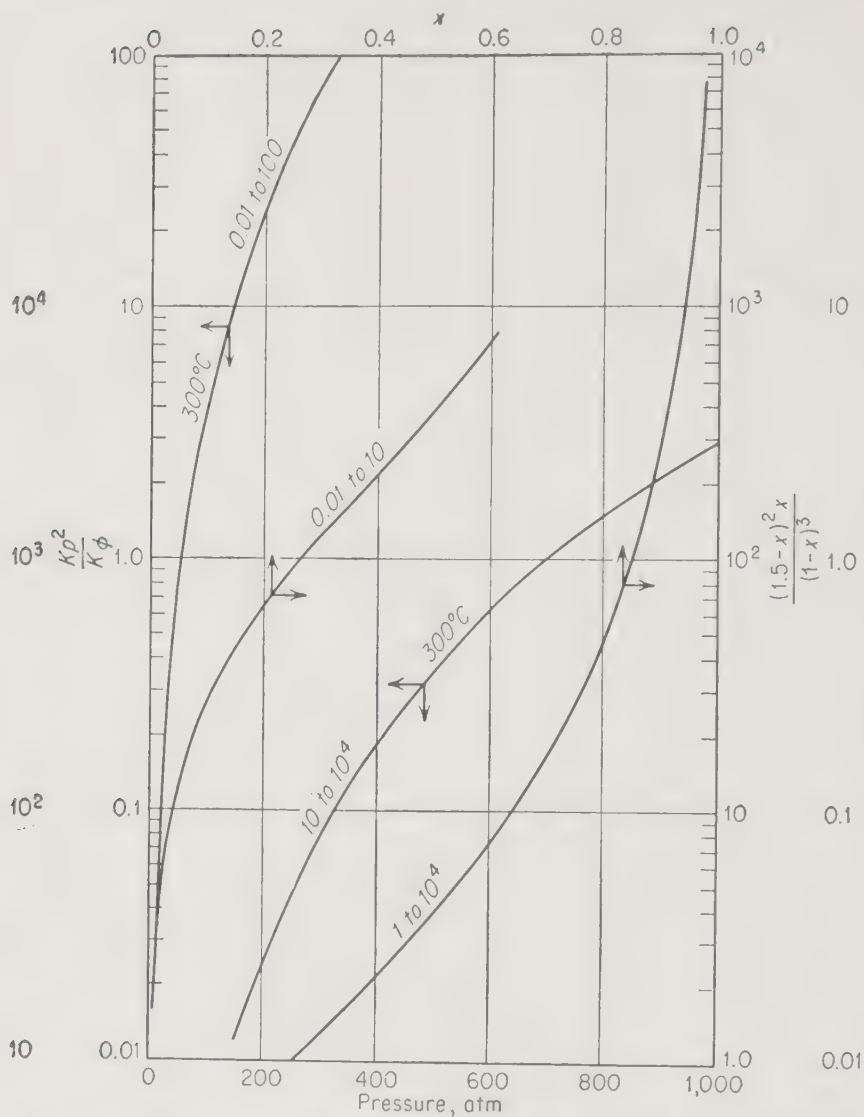


FIG. 10-3. Method of calculating the equilibrium conversion for the reaction $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$.

TABLE 10-1. CALCULATED MOLE PER CENT AT EQUILIBRIUM

Temp., °C	p , atm	K_ϕ	Kp^2/K_ϕ	x	CH_3OH , %	H_2 , %	CO , %
250	100	0.47	34.7	0.77	53	31.3	15.7
	300	0.17	862	0.93	81.5	12.3	6.2
	500	0.10	4,070	0.96	89	7.3	3.7
350	100	0.70	0.635	0.20	7.7	61.5	30.8
	300	0.345	11.8	0.66	39.3	40.5	20.2
	500	0.22	48.4	0.80	57	28.7	14.3
450	100	0.79	0.0413	0.02	0.7	66.2	33.1
	300	0.495	0.586	0.19	7.3	61.8	30.9
	500	0.35	2.33	0.42	19.5	53.7	26.8

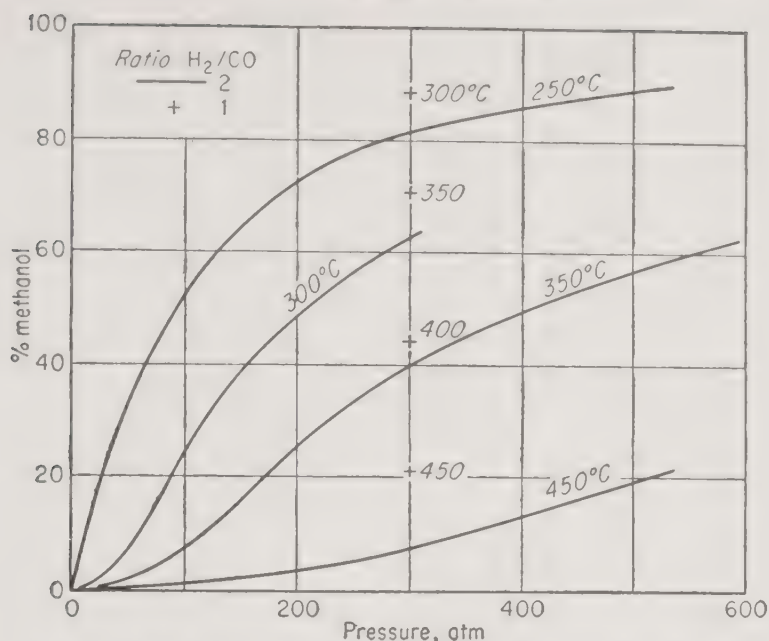


FIG. 10-4. Calculated per cent methanol at equilibrium.

The calculated values for 300°C are tabulated in Table 10-2.

TABLE 10-2

Pressure, atm	x	Mole per cent		
		CO	H ₂	CH ₃ OH
10	0.011	33.2	66.5	0.36
25	0.064	32.6	65.1	2.2
50	0.211	30.6	61.2	8.2
100	0.491	25.2	50.5	24.3
200	0.740	17.1	34.2	48.7
300	0.831	12.6	25.1	62.3
400	0.874	10.1	20.1	69.7
600	0.923	6.7	13.3	79.9
800	0.942	5.2	10.4	84.5
1,000	0.954	4.2	8.4	87.2

The pressure range to 1,000 atm has been covered, based on the assumption that there is no change in volume on mixing the three pure components to form the equilibrium mixture in this pressure range. A volume change undoubtedly occurs. The calculated equilibrium conversion and equilibrium composition probably start to deviate from the true values at pressures of the order of 300 to 500 atm and may be considerably in error at 1,000 atm. Experimental data are not available to determine the accuracy of the prediction at these higher pressures.

Example 10-2. Derive an expression for $\Sigma W'_R$ for the general reaction given by Eq. (10-6) for a reversible process in which the reactants are initially at p_{A_1} , T_{A_1} and p_{B_1} , T_{B_1} and enter the reaction box at p'_A , T' and p'_B , T' , while the product leaves the box at p'_R , T' and is finally brought to the condition p_{R_2} , T_{R_2} . The surroundings are at the temperature T_0 . Express this relation in terms of fugacity, and convert it to include the equilibrium constant K . Show that this result reduces to Eq. (10-22) when $T_0 = T' = T_{A_1} = T_{B_1} = T_{R_2}$.

Solution. The work of compression for the reversible process of bringing the reactant A from T_{A_1} , p_{A_1} to T'_A , p'_A represented in Fig. 10-1 by W_{A_1} at C_A and W_{A_2} at HE_A is given by the following equation. W_{A_1} is the work done by the compressor C_A on the system β , and W_{A_2} is the work done by the heat engine HE_A on the system β in transferring heat from the temperature T_A in C_A to T_0 , reversibly. W_{A_2} is shown by the first integral on the right in the equation, and W_{A_1} by the second integral.

$$W'_A = a \left(- \int_{T_{A_1}, p_{A_1}}^{T', p_{A'}} \frac{T_A - T_0}{T_A} dQ_A + \int_{p_{A_1}, T_{A_1}}^{p_{A'}, T'} v_A dp_A \right)$$

The right-hand side may be replaced by a path consisting of a constant pressure followed by a constant temperature.

$$\begin{aligned} W'_A &= a \left[- \int_{T_{A_1}, p_{A_1}}^{T', p_{A'}} (T_A - T_0) dS_A + \int_{p_{A_1}, T'}^{p_{A'}, T'} v_A dp_A \right] \\ &= a \left[- \int_{T_{A_1}, p_{A_1}}^{T', p_{A'}} (T_A - T_0) dS_A + RT' \ln \frac{\bar{f}_A}{f_{A_1}} \right] \end{aligned}$$

and, extending the same considerations to all products and reactants and including the work from the heat engine acting on the heat of reaction Q ,

$$\begin{aligned} \Sigma W'_R &= - \sum_{i=a,b}^{i=r} i \int_{T_{i_1}, p_{i_1}}^{T', p_{i'}} (T_i - T_0) dS_i \\ &\quad + RT' \left(\ln \frac{\bar{f}_R^r}{\bar{f}_A^a \bar{f}_B^b} - \ln \frac{f_{R_2}^r}{f_{A_1}^a f_{B_1}^b} \right) + \frac{Q(T' - T_0)}{T'} \end{aligned}$$

If the standard states ($f = 1$) are defined for the reaction temperature T' and at p_{A_1} , p_{B_1} , and p_{R_2} , respectively, then $\bar{f}_{A_1} = \bar{f}_{B_1} = \bar{f}_{R_2} = 1$, and from Eq. (10-12) and for a reversible process

$$\begin{aligned} - \sum_{i=a,b}^{i=r} i(E_i - T_0 S_i + p_i v_i) &= \sum W'^{\circ}_R \\ &= - \sum_{i=a,b}^{i=r} i \int_{T_{i_1}, p_{i_1}}^{T', p_{i'}} (T_i - T_0) dS_i + RT' \ln K + \frac{Q(T' - T_0)}{T'} \quad (10-29) \end{aligned}$$

When the temperature is uniform throughout, Eq. (10-29) reduces to Eq. (10-22). When the temperatures of the products and the reactants differ from the equilibrium temperature in the reaction box and from the temperature of the sur-

roundings (system β), Eq. (10-29) indicates that additional terms involving the entropy S and the heat of reaction Q are required to relate the equilibrium constant K to the properties of the reactants and products.

Since K_ϕ for any given reaction is considered independent of the equilibrium composition, it may be represented for that reaction as a function of temperature and pressure. The value of K_ϕ for the methanol reaction



is shown in Fig. 10-2, where

$$K_\phi = \frac{\bar{\phi}_{\text{CH}_3\text{OH}}}{\bar{\phi}_{\text{CO}} \bar{\phi}_{\text{H}_2}^2} \quad (10-31)$$

A similar graph for the ammonia reaction



is shown in Fig. 10-5, where

$$K_\phi = \frac{\bar{\phi}_{\text{NH}_3}}{\bar{\phi}_{\text{N}_2}^{1/2} \bar{\phi}_{\text{H}_2}^{3/2}} \quad (10-33)$$

Effect of Temperature. At constant pressure, the several mole fractions of the reactants and products will adjust themselves as both K and K_ϕ

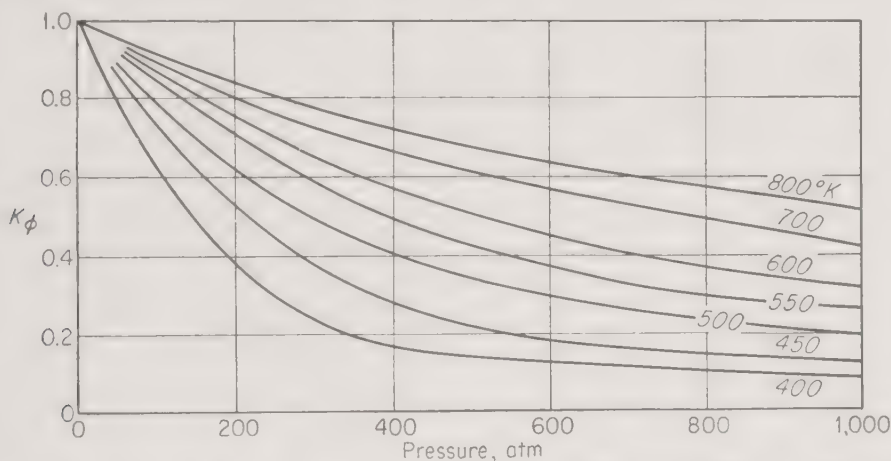


FIG. 10-5. Values of K_ϕ for the reaction $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$. (From O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. II, John Wiley & Sons, Inc., New York, 1947.)

vary with changes in temperature according to Eq. (10-26). The composition of the equilibrium mixture is thus a function of the temperature. A general principle, termed the LeChatelier principle, indicates the direction of the effect of temperature as well as of other variables on the equilibrium conversion of the reaction. According to this principle, if there is a change in any variable which determines the equilibrium composition of the reaction, then the equilibrium will shift in such a direction as to reduce the change in that variable. This principle applied to variations

in temperature indicates that if the reaction gives off heat, an increase in temperature will cause a shift to a lesser equilibrium conversion, reducing the amount of heat given off and thereby the magnitude of the temperature change. Thus an increase in temperature will shift an endothermic reaction in the direction of a greater equilibrium conversion, while it will shift an exothermic reaction in the opposite direction.

Effect of Pressure. The over-all energy requirements for a reversible process depend only on the initial and final states of the reactants and the products and are independent of the temperature and pressure at which the reaction takes place. Changes in pressure do not cause variation in K . But the pressure enters directly in Eq. (10-26) whenever the reaction results in an increase or decrease in the total number of moles of gas present in the system. Under these conditions, the composition of the equilibrium mixture changes with pressure. In general, this effect is such that when the reaction proceeds with an increase in the moles of gas in the system, an increase in pressure will change the equilibrium composition so as to reduce the conversion of the reaction. In this case the exponent on the total pressure is greater than zero. When the moles of gas decrease with the reaction, the exponent on the pressure is less than zero, and an increase in pressure will increase the equilibrium conversion of the reaction. The pressure term reduces to unity when the reaction produces no change in the number of moles, but change in pressure may even then alter the equilibrium composition by causing a change in K_ϕ . This effect of pressure is in accord with the LeChatelier principle.

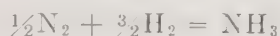
Effects of Inert Gas as a Diluent

Example 10-3. In the synthesis of ammonia, small percentages of inert gases such as methane, helium, and other rare gases are present in the make-up gas fed to the reaction system. As the mixture is recycled, these percentages increase to a limit set by the quantity of gas purged from the system. For a mixture of hydrogen and nitrogen in the molal ratio of 3:1 with various percentages of inert gas, calculate the equilibrium conversion to ammonia and the per cent ammonia in the equilibrium mixture when equilibrium is attained at 700°K and 300 atm. Under these conditions, $K = 0.0091$ and $K_\phi = 0.72$.

Solution. Basis: 1.0 mole initial mixture. Let a = moles inert in initial mixture and x = moles ammonia in equilibrium mixture.

	<i>Initial mixture</i>	<i>Equilibrium mixture</i>
Moles inert	a	a
Moles $N_2 + H_2$	$1 - a$	$1 - a - 2x$
Moles H_2	$\frac{3}{4}(1 - a)$	$\frac{3}{4}(1 - a) - \frac{3}{2}x$
Moles N_2	$\frac{1}{4}(1 - a)$	$\frac{1}{4}(1 - a) - \frac{1}{2}x$
Moles NH_3	0	x
Total	1	$1 - x$

Then from Eq. (10-26) for the reaction,



$$\text{Let } F(x) = \frac{\frac{x}{1-x}}{\left(\frac{\frac{1}{4} - a/4 - x/2}{1-x}\right)^{1/2} \left(\frac{\frac{3}{4} - \frac{3}{4}a - \frac{3}{2}x}{1-x}\right)^{3/2}} = \frac{0.0091 \times 300}{0.72} = 3.79$$

TABLE 10-3

a	$F(x)$	x	Conversion, %	NH ₃ , %
			$100x/[1/2(1-a)]$	$100x/(1-x)$
0.01	$\frac{x(1-x)}{(0.2475 - x/2)^{1/2}(0.7425 - \frac{3}{2}x)^{3/2}}$	0.290	58.6	40.9
0.05	$\frac{x(1-x)}{(0.2375 - x/2)^{1/2}(0.7125 - \frac{3}{2}x)^{3/2}}$	0.274	57.8	37.8
0.10	$\frac{x(1-x)}{(0.225 - x/2)^{1/2}(0.675 - \frac{3}{2}x)^{3/2}}$	0.254	56.5	34.1
0.25	$\frac{x(1-x)}{(0.1875 - x/2)^{1/2}(0.5625 - \frac{3}{2}x)^{3/2}}$	0.197	52.7	24.6
0.50	$\frac{x(1-x)}{(0.125 - x/2)^{1/2}(0.375 - \frac{3}{2}x)^{3/2}}$	0.111	44.5	12.5

The calculations in Table 10-3 show that the per cent conversion decreases with increasing inert content, but the per cent ammonia in the equilibrium mixture decreases more rapidly. This effect is shown in Fig. 10-6.

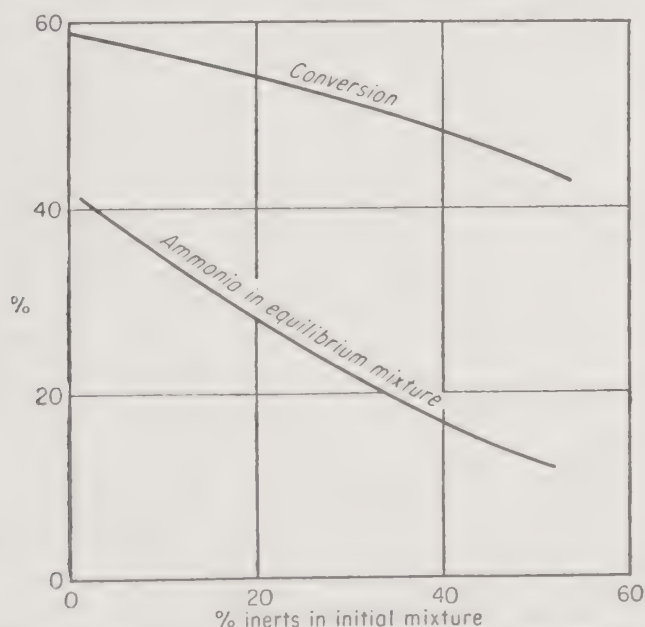


FIG. 10-6. Effect of inert diluents in the initial mixture on per cent conversion and per cent ammonia at equilibrium.

Effect of Nonstoichiometric Ratio of Reactants

Example 10-4. For the same reaction and under the same equilibrium temperature and pressure as in Example 10-3, consider the effect of varying the amount of hydrogen in the reacting mixture to other than the stoichiometric ratio of 3 moles of hydrogen to 1 mole of nitrogen. Calculate the equilibrium conversion and the per cent ammonia in the equilibrium mixture.

Solution. Basis: 1.0 mole of initial mixture. Let a = moles H_2 in the initial mixture and x = moles NH_3 in the equilibrium mixture.

	<i>Initial mixture</i>	<i>Equilibrium mixture</i>
Moles H_2	a	$a - \frac{3}{2}x$
Moles N_2	$1 - a$	$1 - a - x/2$
Moles NH_3	0	x
Total	1	$1 - x$

$$F(x) = \frac{x(1-x)}{(1-a-x/2)^{1/2}(a-\frac{3}{2}x)^{3/2}} = 3.79$$

TABLE 10-4

a	x	Conversion, %	Ammonia, %
		$100x/2(1-a)$	$100x/(1-x)$
0.95	0.098	98.0	10.9
0.90	0.186	93.0	22.9
0.85	0.252	84.0	33.7
0.80	0.286	71.5	40.1
		$100x/2\frac{2}{3}a$	
0.75	0.295	59.0	41.9
0.70	0.289	62.1	40.7
0.60	0.285	64.6	34.8
0.40	0.174	65.5	21.1
0.20	0.0806	60.4	8.8
0.05	0.0154	46.4	1.57

The effect of variation in the percentage of hydrogen in the initial mixture is shown in Table 10-4 and in Fig. 10-7. At compositions near the stoichiometric ratio, the per cent conversion increases as the per cent hydrogen increases or decreases from this composition, but the per cent ammonia in the equilibrium mixture decreases.

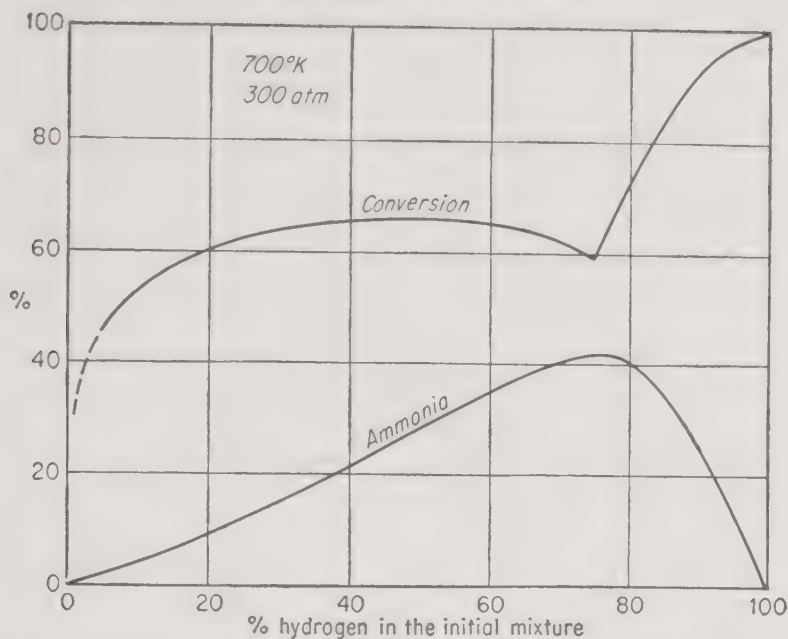


FIG. 10-7. Variation in per cent conversion and per cent ammonia at equilibrium over a range of per cent hydrogen in the initial mixture at 700°K and 300 atm.

Effect of Accumulation of Product

Example 10-5. A mixture in the proportion of 3 moles hydrogen to 1 mole nitrogen is combined with various percentages of ammonia and brought to equilibrium at 700°K and 300 atm. Calculate the per cent conversion and per cent ammonia at equilibrium as a function of the per cent ammonia in the initial mixture.

Solution. Basis: 1 mole initial mixture. Let a = moles ammonia in initial mixture and x = moles ammonia at equilibrium.

	Initial mixture	Equilibrium mixture
NH ₃	a	x
H ₂	$\frac{3}{4}(1 - a)$	$\frac{3}{4}(1 - a) - \frac{3}{2}(x - a)$
N ₂	$\frac{1}{4}(1 - a)$	$\frac{1}{4}(1 - a) - \frac{1}{2}(x - a)$
Total	1	$1 - x + a$
$\frac{x(1 + a - x)}{[\frac{1}{4}(1 + a) - \frac{1}{2}x]^{\frac{1}{2}}[\frac{3}{4}(1 + a) - \frac{3}{2}x]^{\frac{3}{2}}} = 3.79$		

With increasing percentages of ammonia in the initial mixture, the per cent conversion decreases as shown in Table 10-5 and in Fig. 10-8, becoming zero at 41.9 per cent ammonia. The per cent ammonia at equilibrium remains constant at this value and is independent of the amount of ammonia in the initial mixture.

10-5. Mixtures of Real Gases. The direct measurement of the composition of a mixture at chemical equilibrium at high pressure has been made in only a few cases. This composition must usually be calculated.

Equation (10-26) furnishes a basis for making this calculation provided the correct value of K_ϕ can be found. K_ϕ was calculated by using the Lewis and Randall fugacity rule in the preceding examples. This rule is based on the assumption that the equilibrium mixture is an ideal mixture. In such a case, K_ϕ is independent of the composition of the mixture, depending only on pressure and temperature. Mixtures of real gases are frequently not ideal, and K_ϕ then depends on the composition of the mixture as well as on the temperature and pressure.

TABLE 10-5

<i>a</i>	<i>x</i>	Conversion, %	Ammonia, %
		$100 \times 2(x - a)/(1 - a)$	$100x/(1 + a - x)$
0	0.295	59.0	41.9
0.05	0.310	54.7	41.9
0.15	0.339	44.4	41.9
0.30	0.384	24.0	41.9
0.40	0.414	3.5	41.9

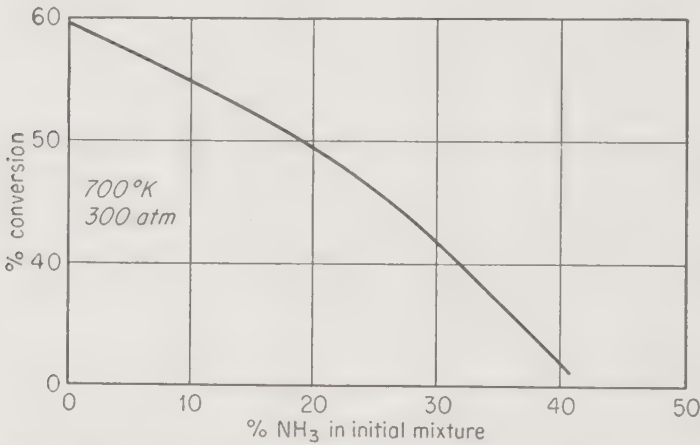


FIG. 10-8. Decrease in per cent conversion with increasing percentages of product ammonia in the initial mixture at 700°K and 300 atm.

A more accurate value of K_ϕ than that from the Lewis and Randall rule may be calculated by a method based on the assumption that the effect of composition may be determined from the properties of the pure components. In the general case, this assumption will not be adequate and further information on the properties of mixtures of the various components must be used. If sufficient information on the components and their mixtures is available, K_ϕ may be calculated in a completely rigorous manner. The information necessary for such a calculation is seldom available. Even when it is available, the calculation becomes involved

when the interaction of the components in all possible combinations is taken into account.

There are at least two methods for determining the effect of composition on the fugacity coefficients in a mixture from the properties of the pure components. These depend on either the graphical correlations based on the theorem of corresponding states or on an equation of state used to represent the behavior of each component and also of the mixture. These methods are readily adapted to the calculation of K_ϕ .

The first method to be described is based on Joffe's⁸ method for determining the fugacities in mixtures. The fugacity coefficient for each component is given by Eq. (8-135). The expressions for $\ln \bar{\phi}_i$ are substituted in Eq. (10-25) which is expressed in the form

$$\ln K_\phi = r \ln \bar{\phi}_R - a \ln \bar{\phi}_A - b \ln \bar{\phi}_B \quad (10-25a)$$

It follows that

$$\begin{aligned} \frac{\ln K_\phi}{r-a-b} = \ln \phi_m + & \left(T'_c - \frac{r}{r-a-b} T_{c_R} + \frac{a}{r-a-b} T_{c_A} \right. \\ & \left. + \frac{b}{r-a-b} T_{c_B} \right) \frac{H^* - H}{RTT'_c} + \left(p'_c - \frac{r}{r-a-b} p_{c_R} + \frac{a}{r-a-b} p_{c_A} \right. \\ & \left. + \frac{b}{r-a-b} p_{c_B} \right) \frac{z-1}{p'_c} \quad (10-34) \end{aligned}$$

The equilibrium composition is calculated from Eqs. (10-26) and (10-34) by a trial-and-error method consisting of the following steps.

1. Choose an arbitrary value of K_ϕ , or determine a preliminary value using the Lewis and Randall fugacity rule.

2. From Eq. (10-26) calculate the equilibrium composition corresponding to this value of K_ϕ .

3. Use the composition from step 2 to calculate the pseudocritical temperature T'_c , the pseudocritical pressure p'_c , the pseudoreduced temperature T/T'_c , and the pseudoreduced pressure p/p'_c . The two latter values give ϕ_m , the fugacity coefficient of the mixture, from Fig. 8-17; $(H^* - H)/T'_c$ from Figs. 8-18 or 8-19; and z from Figs. 8-7, 8-8, or 8-9. By substituting these values in Eq. (10-34), a new K_ϕ is calculated. This value of K_ϕ is used in step 1, and the procedure is repeated. The method converges rapidly in two or three complete cycles of the three steps.

The composition of the equilibrium mixture for the ammonia-synthesis reaction was measured by Larson and Dodge.⁹ Their results may be compared with the methods of calculation already described. Figure

⁸ J. Joffe, *Ind. Eng. Chem.*, **40**:1738 (1948).

⁹ A. T. Larson and R. L. Dodge, *J. ACS*, **45**:2918 (1923); A. T. Larson, *ibid.*, **46**:367 (1924).

10-9 shows the variation in K_p at 450°C from 0 to 1,000 atm when calculated from Eq. (10-27) at the composition observed by Larson and Dodge. The variation of the product of K_p and K_ϕ , the latter determined from the Lewis and Randall fugacity rule,² is shown by the curve marked $K_p K'_\phi$. K''_ϕ is evaluated by Joffe's method, and the product $K_p K''_\phi$ shows considerably less variation.⁸ Joffe's method involves reading a number of charts and is susceptible to multiple errors from this source.

The equation of state proposed by Redlich and Kwong³ and represented by Eq. (8-17) may be used to calculate the equilibrium composition. This has been used to express the fugacity coefficient $\bar{\phi}_i$ for the i th

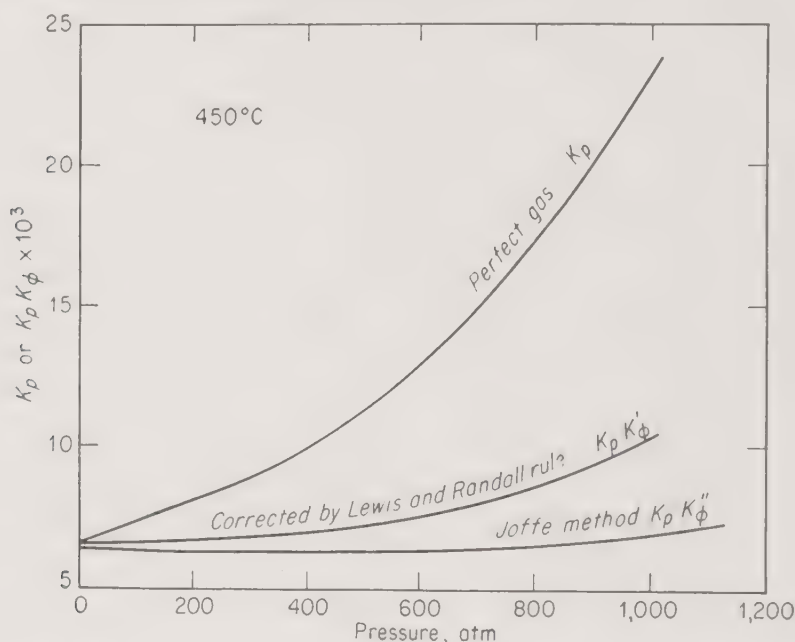


FIG. 10-9. Variation of equilibrium constants with pressure comparing three methods of calculating the behavior of mixtures in the ammonia synthesis equilibrium.

component in a mixture as Eq. (8-136). This equation may be solved for $\bar{\phi}_i$ by using Figs. 8-47 to 8-49 or with the help of Appendix B. A trial-and-error method for calculating the equilibrium composition similar to that used with the Joffe equation consists of the following steps:

1. Choose an arbitrary value of K_ϕ , or determine a preliminary value using the Lewis and Randall fugacity rule.
2. Calculate the equilibrium composition corresponding to this value of K_ϕ from Eq. (10-26).
3. Determine the constants in the Redlich and Kwong equation for each of the pure components in the equilibrium mixture using Eqs. (8-21) and (8-22). (Alternatively, these constants may be determined by fitting Eq. (8-20) to experimental pVT data on each pure component when this is available.)

4. The constants A_j and B_j for the pure components are combined according to Eq. (8-114) to give the constants A and B for the mixture. These are used with Eq. (8-136) and the corresponding charts or tables to give the value of $\bar{\phi}_i$ for each component. The values of $\bar{\phi}_i$ are used to calculate a new value of K_ϕ according to Eq. (10-26), and the series of steps is repeated until the value of K_ϕ does not change.

NOMENCLATURE

- A Work function $E - TS$
- a Moles of reactant A which reacts in stoichiometric proportion; b , moles of reactant B; r , moles of product R formed
- E_{A_1} Molal internal energy of reagent A in initial state; E_{B_1} , of reagent B in initial state; E_{R_2} , of product R in final state
- \mathcal{E}_α Internal energy of system α ; \mathcal{E}_β , of system β
- F Molal free energy, $E + pv - TS$; F° , molal free energy in the standard state
- ΔF $rF_{R_2} - aF_{A_1} - bF_{B_1}$, change in free energy for reaction
- ΔF° Change in free energy for reaction when reagents and products are in their standard states, $rF_{R_2}^\circ - aF_{A_1}^\circ - bF_{B_1}^\circ$
- f_{A_1} Fugacity of pure reagent A in initial state; f_{B_1} , of reagent B in initial state; f_{R_2} , of reagent R in final state
- \bar{f}_A Fugacity of component A in equilibrium mixture at the temperature and pressure of the reaction; \bar{f}_B , of component B; etc.
- f_A° Fugacity of component A in its standard state (equal to 1)
- H Molal enthalpy $E + pv$; H^* , molal enthalpy at a low pressure where the substance is a perfect gas
- K $\bar{f}_R/\bar{f}_A^a\bar{f}_B^b$, equilibrium constant
- K_p $(y_R/y_A^a y_B^b)p^{r-a-b}$, equilibrium constant for a mixture of perfect gases
- K_ϕ $\bar{\phi}_R/\bar{\phi}_A^a\bar{\phi}_B^b$
- p_{A_1} Pressure of reagent A in initial state; p_{B_1} , of reagent B in initial state; p_{R_2} , of product R in final state
- p_α Pressure in system β or in the surroundings
- p'_A Pressure of component A in equilibrium with the reaction mixture through a membrane permeable only to A; p'_B , for B; etc.
- p_c Critical pressure of a pure substance
- p'_c Pseudocritical pressure of a mixture
- Q Heat added to system β ; Q_A , to reagent A; etc.; Q = heat of reaction at constant pressure added to the surroundings
- R Gas-law constant
- r See a
- S_{A_1} Molal entropy of reagent A₁ in initial state; S_{B_1} , of reagent B in initial state; S_{R_2} , of product R in final state
- S_α Entropy of system α ; S_β , of system β
- T Absolute temperature
- T_β Temperature of system β or temperature of the surroundings, °K or °R

T_{A1}	Temperature of reagent A in initial state; T_{B1} , of reagent B in initial state; T_{R2} , of product R in final state, °K or °R
T''	Reaction temperature
T_c	Critical temperature of a pure substance
T'_c	Pseudocritical temperature of a mixture
v_{A1}	Molal volume of reagent A in initial state; v_{B1} , of reagent B in initial state; v_{R2} , of product R in final state
W	Work done on system β and by system α
W'	Work of compression and other work associated with a chemical reaction exclusive of p_v work
$\Sigma W'_R$	Work W' for the reversible reaction; $\Sigma W'^{\circ}_R$, when reagents and products are in their standard states.
W''	Work of compression and other work associated with a chemical reaction exclusive of the p_0v work done by the surroundings
x	Moles of product per mole of unreacted mixture
y_A	Mole fraction of A in a mixture; y_B , of B; etc.
z	Compressibility factor p_v/RT
ϕ_m	Fugacity coefficient for a mixture
ϕ_A	Fugacity coefficient of component A in a mixture [see Eqs. (8-124) and (8-125)]

CHAPTER 11

CHEMICAL REACTORS

A definite amount of one or more chemical substances subjected to a given set of conditions is called a system. These substances may react to form new substances as products. This change in the system is a chemical process. When the system has no tendency to react under the imposed conditions, it is at equilibrium. In Chap. 10 thermodynamics was used to predict (*a*) the nature of a system at equilibrium, (*b*) whether a chemical process could take place, and (*c*) the energy required by or given off from the system. However, thermodynamics is of no value in determining the size and design of the reactor for the chemical process. It may one day be possible to predict these from a knowledge of the intermolecular forces, statistical mechanics, kinetic theory, and the statistical distribution of certain solid structures. Marked progress has been made in recent years toward a quantitative formulation of the principles of reaction kinetics for use in reactor design. These methods are usually too complex as yet for the design of commercial reactors. A combination of theoretical reaction kinetics with empirical methods applied to reaction rates will be described.

A chemical reaction, like all natural processes, is a spontaneous change. That is, all processes take place as a result of a tendency to change. This tendency may be called a driving force. When equilibrium is attained, the driving force is zero and no further change will occur. The difference between an existing state and equilibrium thus represents the magnitude of the driving force. The rate at which a process takes place depends not alone on the magnitude of the driving force but also on the amount of resistance to the change. Water tends to flow from a faucet because of the difference between the pressure in the pipe and atmospheric pressure. The greater this difference in pressure, the greater the driving force tending to cause flow, but the rate of flow depends also on how wide the faucet is opened. The small hole through the faucet constitutes a resistance which limits the rate of flow. If the faucet is closed, the tendency to flow is still present but no flow takes place. A similar situation exists in an electric circuit. A large difference in voltage represents a large driving force, but the flow of current depends equally on the electric resistance

in the circuit. The resistance to a chemical change often appears more vague than the resistance in the examples cited above, but it is none the less as real.

Some reactions proceed to equilibrium so rapidly that the rate of reaction can scarcely be measured. This is true of most ionic reactions in solution. Other reactions proceed more slowly or not at all in spite of a favorable tendency to react. An understanding of the factors which modify the reaction rate will serve as a tool to use in speeding up a desirable reaction or in avoiding an undesirable one. The means available for doing this in reactions of commercial importance include the control of temperature, pressure, and concentration, the use of catalysts or inhibitors, and variations in the design of and flow conditions in the reaction vessel. The choice of these conditions is based on the most favorable economics and not necessarily on obtaining the most nearly complete reaction.

11-1. Homogeneous Reactions. A reaction which takes place wholly in a single phase is known as a homogeneous reaction. Such reactions may occur in either a liquid or a gas phase. Frequently a reaction which was at first thought to occur in the main body of a fluid is later found to take place on the walls of the container. A reaction which takes place at a solid-fluid interface is known as a heterogeneous reaction. The solid surface may be the wall of the reaction vessel, or packing material or catalysts added for the purpose of furthering the reaction. The reaction may occur partially in the main body of the fluid and partially at the solid-fluid interface. It is then partly homogeneous and partly heterogeneous. One type may be distinguished from the other by varying the ratio of the solid-surface area to the volume of the reactor. The rate of a homogeneous reaction is independent of this ratio, while that of a heterogeneous reaction is proportional to it. When the reaction is partially homogeneous and partially heterogeneous, the rate of the former may be obtained by extrapolating the rate to zero ratio of surface to volume.

Order of Reactions. Some understanding of the kinetics of a reaction may be acquired by starting with a simple concept or assumption and later modifying this as a result of comparison with experimental facts. Such a simple concept considers that a homogeneous reaction takes place as a result of molecular collisions according to the stoichiometrical equation for the reaction. Consider the general equation



This is a stoichiometric equation. According to this equation, a molecules of A, b molecules of B, and c molecules of C collide simultaneously and react to form r molecules of R plus s molecules of S. Let the reaction mixture consist initially at time $\tau = 0$ of N_{A0} mols of A, N_{B0} of B, and

N_{C0} of C, and at any later time τ it consists of N_A mols of A, N_B of B, and N_C of C. The rate of decrease of A may be taken as a measure of the rate of reaction since the rate of decrease of B and C must be in stoichiometrical proportion.¹ Choose as a basis 1 mole of A at time τ , and then the rate of reaction may be expressed as the ratio of the rate of change of N_A per mole of N_A , or $dN_A/N_A d\tau$. This will be termed the proportional rate of reaction. For one molecule of A to react, it must collide with $(a - 1)$ molecules of A, and with b and c molecules of B and C, respectively. The rate of disappearance of A is proportional to the number of these collisions, which depends on the number of each kind of molecule per unit volume, as expressed by the equation

$$\frac{dN_A}{N_A d\tau} = -f \left(\frac{N_A}{V} \right)^{a-1} \left(\frac{N_B}{V} \right)^b \left(\frac{N_C}{V} \right)^c \dots \quad (11-2)$$

The ratios N_A/V , N_B/V , and N_C/V are the concentrations of the reactants as moles per unit volume. If the reactants and products are approximately perfect gases, then $V = nRT/p$, where n is the total moles of gas present—reactants, products, and inerts. Substituting in Eq. (11-2),

$$\begin{aligned} \frac{dN_A}{N_A d\tau} &= -f \left(\frac{N_A p}{nRT} \right)^{a-1} \left(\frac{N_B p}{nRT} \right)^b \left(\frac{N_C p}{nRT} \right)^c \\ &= \frac{-f'}{(nRT)^{a-1+b+c}} N_A^{a-1} N_B^b N_C^c p^{a-1+b+c} \end{aligned} \quad (11-3)$$

where f is a function of temperature.

When b and c are zero and a is unity, the reaction is called a *first-order* reaction. Then

$$\frac{dN_A}{N_A d\tau} = -f \quad (11-4)$$

and the proportional rate of reaction is independent of the concentration of A and of the total pressure and depends on the temperature only. The order of the reaction is defined as $a + b + c$. Reactions of the first and second order are common. Third-order reactions have been identified, but none of higher orders are known.

If the reaction is carried out at *constant volume*,

$$\frac{dN_A}{N_A} = \frac{V dN_A}{V N_A} = \frac{d(N_A/V)}{N_A/V}$$

and c_A may be substituted for N_A/V , c_B for N_B/V , etc. Then Eq. (11-2), when restricted to a reaction at constant volume, becomes

$$\frac{dc_A}{d\tau} = -f c_A^a c_B^b c_C^c \quad (11-5)$$

¹ T. K. Sherwood and C. E. Reed, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1939.

Without this restriction, Eq. (11-2) can be put in the form

$$\frac{dc_A}{d\tau} = -f c_A^a c_B^b c_C^c - \frac{c_A}{V} \frac{dV}{d\tau} \quad (11-6)$$

for comparison with Eq. (11-5). Since Eq. (11-5) is for constant volume it is not applicable to reactions at constant pressure unless the total moles of reactants remains constant, that is,

$$a + b + c + \dots = r + s + \dots$$

Both volume and pressure are then constant if the temperature is constant.

When the reaction is reversible, A will be formed by reaction between the products R and S, and, on a basis of 1 mole of R,

$$\frac{dN_R}{N_R d\tau} = -f' \left(\frac{N_R}{V} \right)^{r-1} \left(\frac{N_S}{V} \right)^s \quad (11-7)$$

but $dN_A = -(a/r) dN_R$, and, converting to a basis of 1 mole of A, the proportionate rate of the reverse reaction is

$$\frac{dN_A}{N_A d\tau} = \frac{af'}{r} \frac{N_R}{N_A} \left(\frac{N_R}{V} \right)^{r-1} \left(\frac{N_S}{V} \right)^s \quad (11-8)$$

or the net proportional rate of disappearance of A is

$$\frac{dN_A}{N_A d\tau} = \frac{a}{r} f' \frac{N_R}{N_A} \left(\frac{N_R}{V} \right)^{r-1} \left(\frac{N_S}{V} \right)^s - f \left(\frac{N_A}{V} \right)^{a-1} \left(\frac{N_B}{V} \right)^b \left(\frac{N_C}{V} \right)^c \quad (11-9)$$

At equilibrium the change in N_A is zero and

$$\frac{r}{a} \frac{f'}{f} = K_c = \frac{\frac{N_R}{V} \left(\frac{N_R}{V} \right)^{r-1} \left(\frac{N_S}{V} \right)^s}{\frac{N_A}{V} \left(\frac{N_A}{V} \right)^{a-1} \left(\frac{N_B}{V} \right)^b \left(\frac{N_C}{V} \right)^c} = \frac{c_R^r c_S^s}{c_A^a c_B^b c_C^c} \quad (11-10)$$

where K_c is the equilibrium constant based on concentrations. It follows that

$$K_c = \frac{N_R^r N_S^s}{N_A^a N_B^b N_C^c} \left(\frac{p}{nRT} \right)^{r+s-a-b-c} \quad (11-11)$$

and since K_c is independent of pressure for perfect gases, the number of moles of each component at equilibrium will vary with the total pressure when $r + s - a - b - c$ is not zero.

The kinetics of reactions is not often in accord with the mechanism indicated by the stoichiometric equation. While reactions take place

following collision of the reactants, it is now known that a much more restricted set of conditions is necessary than that visualized in the simple collision concept just described. The mechanism is likely to be further complicated because the reaction takes place in a number of steps with the final product resulting from the combination of molecules or elements not shown in the stoichiometric equation. The stoichiometric equation thus gives little information as to the nature of the reaction or its order as defined above. Measurements of the rate of the reaction are used to determine the order of the reaction. When a reaction has been shown by experiment to be of the first order, it is spoken of as a monomolecular reaction. Second- and third-order reactions are called bimolecular and trimolecular. Frequently, when a reaction takes place in a number of steps, one of these is much slower than the others. This step then determines the order of the reaction. Methods for determining the order of a reaction from measurements of the rate of reaction are given in other texts.^{2,3}

Arrhenius Equation. The analysis of experimental rate-of-reaction measurements leads to values of the constant f in Eq. (11-3) at various temperatures. Arrhenius⁴ proposed the equation

$$f = ae^{-Q/RT} \quad (11-12)$$

This equation represents the effect of temperature on the reaction-rate constant f . According to the concept supporting this equation, Q is called the activation energy. It may be determined from a plot of $\ln f$ vs. $1/T$. This results in a straight line with a slope of $-Q/R$. a is a constant.

It was realized long ago that not all reactant molecules which collide in the course of their movements, in accord with the kinetic theory, react with each other. It was then proposed that only those molecules reacted which had acquired energy in excess of the average molecules. Since energy is not distributed uniformly among the molecules but according to a statistical distribution, a small percentage of the molecules will possess rather high energies. This distribution of energy is shown in Fig. 11-1.⁵ The fraction of the molecules in a given mixture with high energy content is small but appreciable. When a few molecules attain a sufficiently high energy level, they will react on collision even though other molecules with lower energy contents will not react. Q is the

² O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. III, Kinetics and Catalysis, John Wiley & Sons, Inc., New York, 1947.

³ J. M. Smith, "Chemical Engineering Kinetics," McGraw-Hill Book Company, Inc., New York, 1956.

⁴ S. Arrhenius, *Z. physik. Chem.*, **4**:226 (1889).

⁵ F. Daniels, *Ind. Eng. Chem.*, **35**:504 (1943).

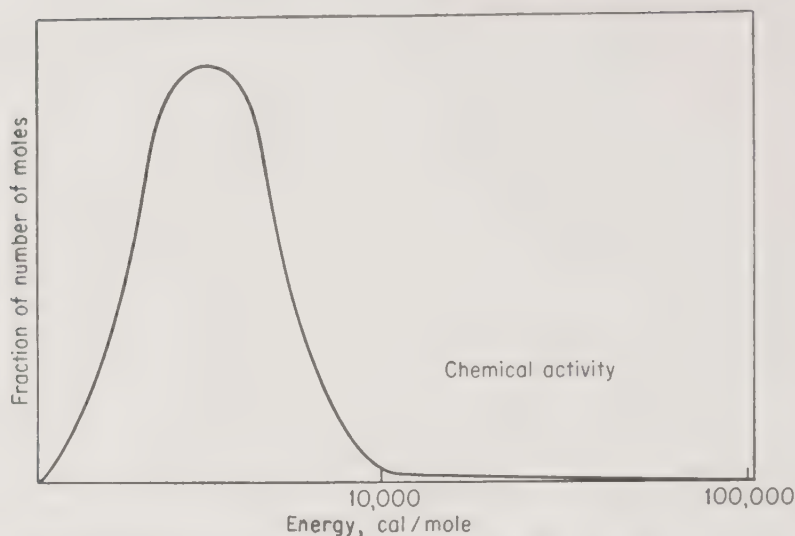


FIG. 11-1. Distribution of energy in a group of molecules. [From F. Daniels, *Ind. Eng. Chem.*, **35**:504 (1943).]

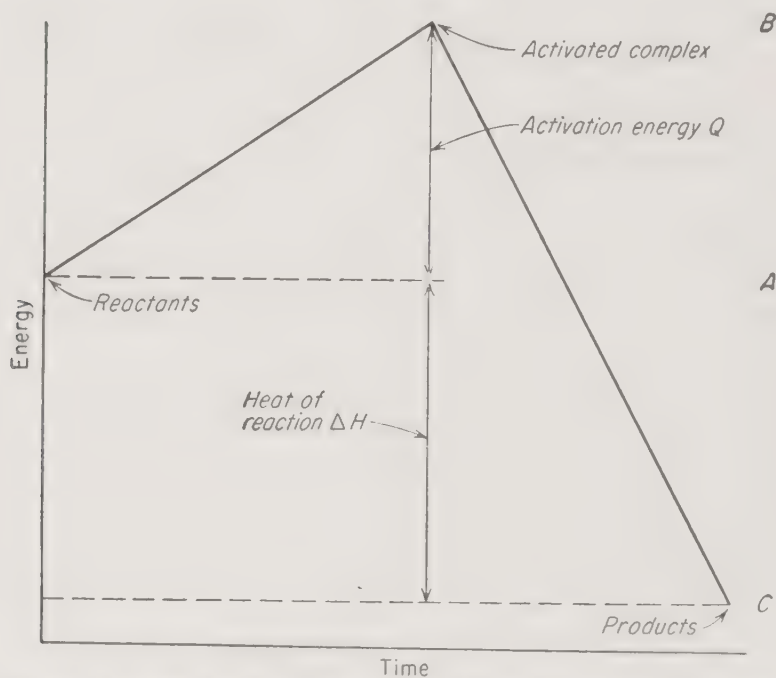


FIG. 11-2. Relation between activation energy and heat of reaction. [From F. Daniels *Ind. Eng. Chem.*, **35**:504 (1943).]

activation energy, or the energy level which must be attained for reaction to take place.

The activation energy bears no direct relation to the heat of reaction. The two are compared in Fig. 11-2 for an exothermic reaction. The reacting molecules acquire their activation energy by collision with the statistically small percentage of molecules having a momentarily high

energy. Although the number of these molecules is small, they are sufficiently numerous to account for the progress of chemical reactions. The number of molecules with high energy increases exponentially with the temperature, which explains the approximate statement that the rates of many chemical reactions double with each 10°C rise in temperature. Referring to Fig. 11-2, the average energy of the reactant molecules is shown by the level *A*. Those molecules which react at any instant must attain the energy level shown at *B*. After reaction, the average energy of the product molecules is shown at *C*. Thus the difference in energy between levels *A* and *C* is the heat of reaction, while that between levels *B* and *A* is the energy of activation.

For an endothermic process, the reaction takes place from right to left with the energy level of the products becoming the energy level of the reactants and that of the reactants replacing the products as shown in Fig. 11-2. The energy of activation for an endothermic process is then the difference between levels *B* and *C*, and this is greater than the heat of reaction which is then between levels *A* and *C*. The Arrhenius equation has been effective when used to determine the activation energy from experimental measurements of the rate of reaction. It permits a correlation of the rate of reaction with temperature.

Theory of Absolute Reaction Rates. The Arrhenius equation and the collision-activation-energy concept have serious limitations. Two of these will be discussed briefly. The first is the difficulty in explaining the mechanism of monomolecular-gas-phase reactions. For this class of reactions, the proportional rate of reaction is independent of the concentration of reacting molecules. That is, the percentage of the reactant molecules which react in any given time interval is independent of the number of these molecules present. On the other hand, the number of collisions is proportional to the square of the concentration, and this would indicate that the concentration of reactant molecules should have an effect on the proportional rate of reaction. No satisfactory explanation for this situation has been obtained from this theory. A second limitation is evidenced by the large discrepancy often found between the number of molecules which react and those which have the necessary energy to react. This discrepancy sometimes amounts to several orders of magnitude and results in predicted reaction rates which are much too large.

A successful formula for predicting reaction rates has been provided by Eyring.⁶ His formula follows directly from statistical mechanics. Its chief limitation is the amount of information needed to apply it to practical commercial reactions. In spite of this limitation, it supplies a sound basis for understanding the factors which control the rate of reaction and

⁶ S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, 1941.

for developing semiempirical equations which are consistent with fundamental concepts.

The Eyring equation is

$$k = \kappa \frac{RT}{\mathfrak{N}h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (11-13)$$

The theory supporting this equation considers that reactions take place in steps. One of these steps consists in the formation of an *activated complex*. The activated complex is an unstable intermediate compound formed from the reactants, which decomposes into the products. The reaction may be thought of as taking place as follows.



An essential part of the theory for homogeneous reactions is the assumption that the activated complex is in thermodynamic equilibrium with the reactants. The first step is thus relatively rapid, and the rate of decomposition of the activated complex to form products determines the rate of the over-all reaction. In Eq. (11-13), ΔS^* is the entropy change for the formation of the activated complex from the reactants and ΔH^* is the enthalpy change for this step—the enthalpy of activation. ΔS^* and ΔH^* are related to $\Delta F^{\circ*}$ and the chemical-equilibrium constant K^* for the formation of the activated complex by the usual equation from thermodynamics,

$$\Delta F^{\circ*} = \Delta H^* - T \Delta S^* = -RT \ln K^* \quad (11-14)$$

and

$$K^* = e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (11-15)$$

Equation (11-13) may be compared with Eq. (11-12), and the term α in the latter is seen to include the first part of the former, including the exponential entropy term [that is, $(\kappa RT/\mathfrak{N}h)e^{\Delta S^*/R}$], while Q is roughly equivalent to ΔH^* .

The comparison of experimentally determined reaction-rate constants with Eqs. (11-13) to (11-15) is frequently complicated by such factors as wall effects, trace catalysts, impurities, and side reactions, consecutive reactions, or reverse reactions, as well as temperature and concentration gradients in the reaction zone.

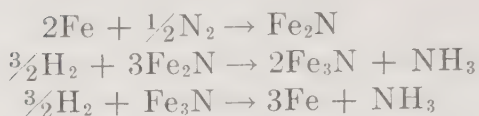
The rate of a given reaction cannot as yet be predicted but must be determined experimentally. The theory of reaction kinetics is useful, however, in interpreting and correlating such measurements and in interpolating or extrapolating them to predict other values. The true equilibrium state is independent of the reaction mechanism and may be predicted by thermodynamics. From a practical standpoint, however, the reaction may approach a pseudoequilibrium state which differs from the

true thermodynamic equilibrium and depends on the reaction mechanism and kinetics.

11-2. Heterogeneous Reactions. Many industrially important chemical reactions take place in the presence of two or three phases. While these phases may be any combination of gas, liquid, or solid, attention will be directed principally to reactions involving combinations of solids and liquids or solids and gases. Heterogeneous reactions between gases and liquids also take place as in carbonylations, hydrocarbonylations, and oxidations employing a dissolved catalyst. Most catalytic reactions are of the heterogeneous type. A *catalyst* is a substance which does not appear in the stoichiometric equation yet has an effect upon the reaction. It increases the rate of a reaction or causes a reaction to take place which otherwise does not proceed. On the other hand, it can have no effect on the true chemical equilibrium. The amount of catalyst is usually small compared to the material which reacts. Similarly, a substance may act as a negative catalyst, or *inhibitor*, and reduce the rate of a reaction which takes place freely in the absence of the inhibitor. This action is to be distinguished from that of a *catalyst poison* which interferes with the action of a catalyst but does not affect a reaction which proceeds without a catalyst.

Mechanism of Reaction. Van der Waals, or capillary, adsorption consists of the attraction of molecules from a gas or vapor to form a layer of loosely held molecules on the surface of a solid. The layer is held by mild molecular or capillary forces. It might at first be supposed that a catalyst acts simply by bringing the reacting molecules together on its surface. A catalyst would then act by *adsorption*, and any good adsorbent should be a good catalyst. Comparison of the action of several adsorbents on a given reaction mixture shows that this simple concept does not give an adequate explanation. Reaction does not take place in proportion to the adsorption efficiency. In fact, one adsorbent may exhibit catalytic activity while another equally good or better adsorbent may have little or no catalytic activity. A specific effect of certain solids for a given reaction is clearly shown by the data. If it were necessary merely to bring the reacting molecules together, this could be done equally well by subjecting them to sufficiently high pressure. Again, this procedure has been tried and found to be ineffective in reproducing the action of a good catalyst.

Another postulate to explain the action of a catalyst is that based on the formation of an *intermediate compound* between the gas and the catalyst. Such compounds have been shown to exist in some cases, but in general the concept falls short of being an adequate explanation. As an example, the synthesis of ammonia on an iron catalyst may conceivably take place according to the reactions



Iron nitride forms in copious amounts at even moderate pressures when ammonia decomposes (to $3\text{H}_2 + \text{N}_2$) on the surface of iron. Yet the nitrides of iron require nitrogen pressures of the order of 5,000 atm for their formation. Thus, it is futile to explain the reaction by this mechanism under ordinary conditions. Yet these reactions may well proceed in the transitory states existing on the catalyst surface.

A third concept is that involving *active points* on the catalyst surface. While the catalyst molecules in general may not be capable of reacting with the gases, certain of these molecules in exposed positions or in positions of strain are visualized as having unsatisfied valence forces which form intermediate compounds with the gas molecules. These intermediate compounds then react further to yield the final product. This latter concept explains a number of the features of catalyst behavior. Frequently a catalyst which is active over a range of temperatures loses this activity at higher temperatures, well below the melting point. An explanation is that a partial *sintering* takes place which relieves the stress around the active points or allows these molecules to recede into the solid surface out of an exposed position. This action reduces the catalyst activity.

Small amounts of certain chemicals can severely reduce the activity of a catalyst. These are catalyst *poisons*. Amounts of these so small that only a sufficient number of molecules is available to react with a small portion of the molecules in the surface layers of the catalyst may seriously reduce catalyst activity. If the catalyst activity is associated with proportionately small numbers of the surface molecules at the active points, then a compound which reacts with or covers these molecules will interfere with the catalytic action.

These theories of catalyst mechanism are not quantitative, and their usefulness in engineering design of reactors or processing equipment is limited. Efforts are being made at the present time to formulate quantitative laws for reaction kinetics. The results are promising, and these will be developed in the following paragraphs. These methods involve the idea of the formation of an *activated complex* as a necessary step in the reaction mechanism. This follows directly from the theory of absolute reaction rates. The activated complex may be formed in heterogeneous reactions by activated adsorption of the reactants on the surface of the catalyst. Activated adsorption differs from van der Waals, or capillary, adsorption because of the nature of the forces holding the adsorbed molecules to the solid surface. In activated adsorption, these

forces are stronger and are similar to those which hold atoms together in molecules.

A large quantity of experimental data obtained in recent years has led to a better understanding of the mechanism of heterogeneous reactions. In reactions involving a gas or liquid phase and a solid catalyst, the true heterogeneous reaction takes place on the surface of the solid. The reactants, along with other molecular species present, are adsorbed on the surface of the catalyst. This adsorption amounts to a loose type of chemical-compound formation and is activated adsorption as distinguished from ordinary van der Waals adsorption and capillary condensation. When the reactant molecules are adsorbed on certain molecules in the surface, they form an activated complex with these catalyst molecules. Those complexes having sufficient energy react further to yield the reaction products. The molecules reacting by way of the activated complex with the catalyst require considerably less activation energy than when reacting by way of the activated complexes formed in a homogeneous mixture. Since the probability of acquiring this lower energy is much greater, more molecules react in a given time in the presence of the catalyst. The actual mechanism of the reaction on the active centers is somewhat more complex than that pictured above. Several possibilities will be mentioned.⁷

In one possible reaction, a single molecule A forms an activated complex with a single catalyst site and then isomerizes according to the reversible reaction



Such a reaction is considered monomolecular. The reverse reaction could take place by the same mechanism.

As another possibility, two molecules react to form a single product by a reversible reaction of the type



In this case it is assumed that A and B are adsorbed on adjacent catalyst sites, and the reaction takes place on the surface in this activated condition to form the single product molecule which breaks away from the two sites simultaneously. The reverse reaction requires that R be adsorbed simultaneously on two adjacent catalyst sites and that these two sites, or one of them and another adjacent one, be vacated before another molecular reaction can take place at this point.

When, as a third possibility, A and B react to form two product molecules R and S,



⁷ O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, **35**:529 (1943).

A and B are separately adsorbed on adjacent sites, and R and S break away individually. These reactions involving two molecules or two sites are bimolecular reactions. Reactions involving three or more molecules and more than two sites are easily conceivable. The more complex activation mechanisms result in slower reaction rates and are probably rare.

The preparation and preliminary treatment of a catalyst are directed toward providing an extensive surface containing the catalyzing elements or compounds at active centers and having the catalyst in a physical or chemical state which readily forms the activated complex. Since the detailed molecular specifications of this state are usually not known, the choice and preparation of a new catalyst are largely empirical. When the catalyst is in use, many factors may decrease its effectiveness. The temperature or pressure of operation may cause physical changes which reduce the number of active sites. Any interference with these sites will produce a similar result. Chemical reaction of the catalyst molecules with an impurity may poison the catalyst. If this reaction is reversible, the poisoning is temporary and the catalytic activity is restored by removing the impurity. Adsorption of inert gases or even preferential adsorption of a single reactant or product may effectively block the reaction sites.

The reactions are not usually those indicated by the stoichiometric equation. Thus a given reaction may take place in a number of steps, only one of which involves activated adsorption on a catalyst. When all steps except the catalytic one take place rapidly, the catalytic step will determine the rate of the reaction. The reaction may take place by one series of steps with one catalyst and by a different series with another catalyst. If the over-all reaction is the same, this difference in reaction mechanism will not alter the thermodynamic equilibrium, but it may have a large effect on the rate of approach to equilibrium.

The above discussion assumes that reactants encounter no resistance in reaching the catalyst surface, or the products in leaving it. The over-all reaction mechanism must take this physical transfer into account. The heat of the reaction must likewise be transferred to or from the catalyst surface. These transfer processes are frequently significant and in the case of a highly reactive catalyst are likely to control the reaction rate. The complete mechanism of reaction in a continuous catalytic gas-solid phase reactor involves the following steps at each point in the reactor⁷ (see Fig. 11-3).

1. The reactants are transferred from the main body of the gas stream to the outer surface of the catalyst particles. In the vicinity of the particle this transfer is by molecular diffusion through a relatively stagnant gas layer of inerts and products, and it results from a partial-pressure

gradient, across this layer, of the diffusing component. With a non-porous catalyst the reactants are now in a position to be adsorbed.

2. In the case of porous catalysts, the reactants must diffuse into the pores in order to reach the extensive internal surface. The *catalytic effectiveness factor*³ is a measure of the importance of this step. It is defined as the ratio of the actual reaction rate per unit mass of catalyst to the rate which would result if no concentration gradients existed within the catalyst particle.

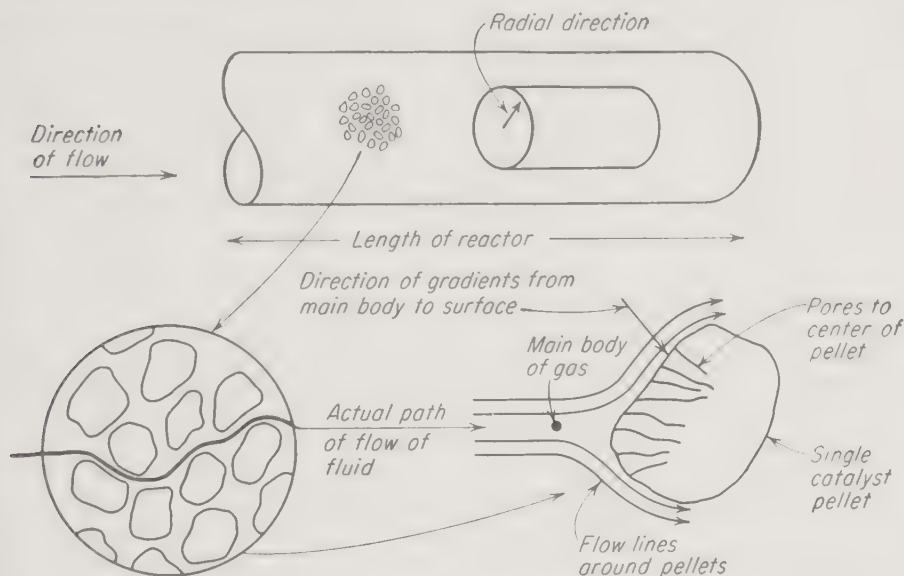


FIG. 11-3. Position of solid grains and fluid paths in a catalyst bed.

3. The reactants are activatedly adsorbed on the catalyst surface.
4. The surface reaction takes place forming activatedly adsorbed products.
5. The activatedly adsorbed products are desorbed from the surface.
6. The products diffuse out of the pore structure to the outer surface of the catalyst particles. This step is not present with nonporous particles.
7. The products diffuse through the stagnant gas layer adjacent to the particles and thence into the main stream of mixed gases.

These transfer and reaction steps proceed throughout the volume of the catalyst bed and result in concentration gradients of reactants and products along the length of the reactor. Similar temperature gradients between the main body of the gas stream and the catalyst surface cause the transfer of the heat of reaction by thermal conduction and convection. When this heat is added or removed, as the case may be, through the reactor walls, a temperature gradient will be set up in a direction normal

³ E. W. Thiele, *Ind. Eng. Chem.*, **31**:916 (1939).

to the walls. If the heat transfer through the reactor walls is not equal to the heat of reaction, the difference will result in a temperature gradient in the direction of gas flow. When there is a temperature gradient normal to the reactor wall, this will result in a variation in the rate of reaction in this direction and gives rise to a concentration gradient of the reactants and products in the radial direction. There will, of course, be no net diffusion to or away from the wall. Resistance to the flow of gas gives rise to a pressure gradient in the direction of gas flow. Schwartz and Smith⁹ have shown that important velocity variations also exist across a packed bed in a pipe. These are shown in Fig. 11-4. Pellets $\frac{1}{4}$ in. in

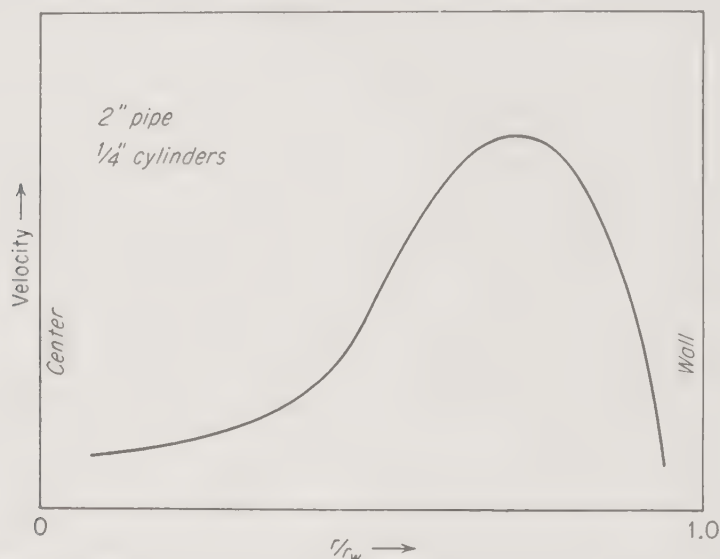


FIG. 11-4. Velocity distribution in a tube filled with catalyst pellets. [From C. E. Schwartz and J. M. Smith, *Ind. Eng. Chem.*, **45**:1209 (1953).]

diameter by $\frac{1}{4}$ in. were placed in a 2-in.-diameter pipe. A maximum axial velocity was observed about three-quarters of the distance from the center line to the wall.

These temperature, pressure, and concentration gradients result in variations in the rate of reaction from point to point in the catalyst bed. While the general picture is complex, it can be greatly simplified by minimizing many of the gradients and transfer resistances by suitable reactor and catalyst design. Equations have been devised for handling a number of the special cases which result when one or more of the steps described are of major importance.^{2,3,10}

Catalysts. When a catalyst is being sought for a given reaction, one might first determine the effectiveness of certain pure compounds. The catalytic activity of these compounds could be compared by observing the

⁹ C. E. Schwartz and J. M. Smith, *Ind. Eng. Chem.*, **45**:1209 (1953).

¹⁰ D. M. Hurt, *Ind. Eng. Chem.*, **35**:522 (1943).

concentration of the final products as a percentage of their concentrations at equilibrium when the conditions for the reaction such as temperature, pressure, concentrations of the reactants, and time of reaction are all kept the same. Different compounds would show varying degrees of catalytic activity. The next step could be to test mixtures of one, two, three, or more compounds. The method of preparation of compounds and their mixtures, as well as the choice of compounds, has a pronounced effect on their activity as a catalyst. Supposing for the moment that a standard method of preparation is adopted, the activity of these mixtures could then be compared. Some compounds would be added for

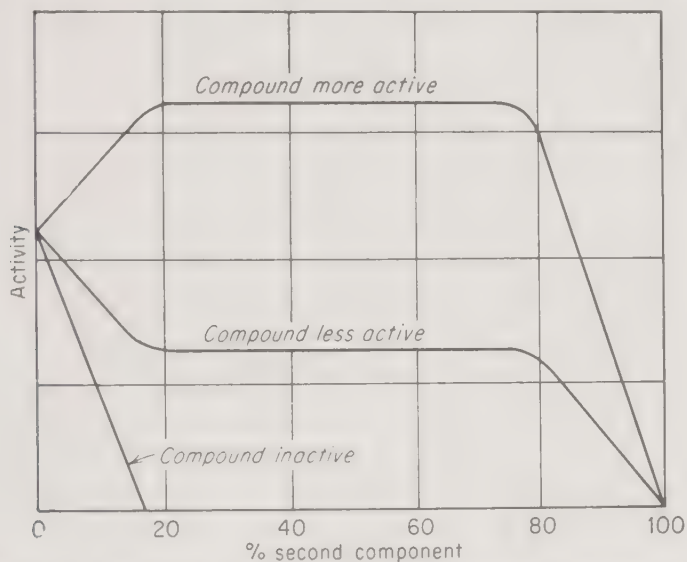


FIG. 11-5. Effect of formation of a compound on catalyst activity. (From R. H. Griffith, *The Mechanism of "Contact Catalysis,"* 2d ed., Oxford University Press, New York, 1946.)

one purpose, others for another. Small amounts of unsuspected elements present in mere traces may have pronounced effects, and these, no doubt, account for some of the confusion which frequently accompanies catalyst development.

A second compound could then be added to the primary compound in such a way as to form a *new compound*.¹¹ The new compound might be completely inactive or more or less active than the primary compound. The effect of increasing percentages of the second compound would then be that shown in Fig. 11-5. A rapid decrease in activity occurs when an inactive compound is formed. This is similar to a poisoning action. Although the second compound has a lower catalytic activity than the first, the new compound may have a greater or lesser activity.

¹¹ R. H. Griffith, *"The Mechanism of Contact Catalysis,"* 2d ed., Oxford University Press, New York, 1946.

An unusual increase in activity may be produced in rather narrow ranges of the percentage of the second compound. This is known as *promoter* action. The promoter may itself be catalytically inactive or have some activity, but in either case it is characterized by a sharp rise in activity at a definite concentration. This effect is shown in Fig. 11-6. On the other hand, added substances may greatly reduce the activity of the primary compound. These are *poisoning* effects. Usually a small amount of poison is sufficient to cause a considerable reduction in catalytic activity. Thus the addition of 0.03 cc of carbon dioxide to a material which had an adsorptive capacity of 1 cc of hydrogen at 1 mm pressure

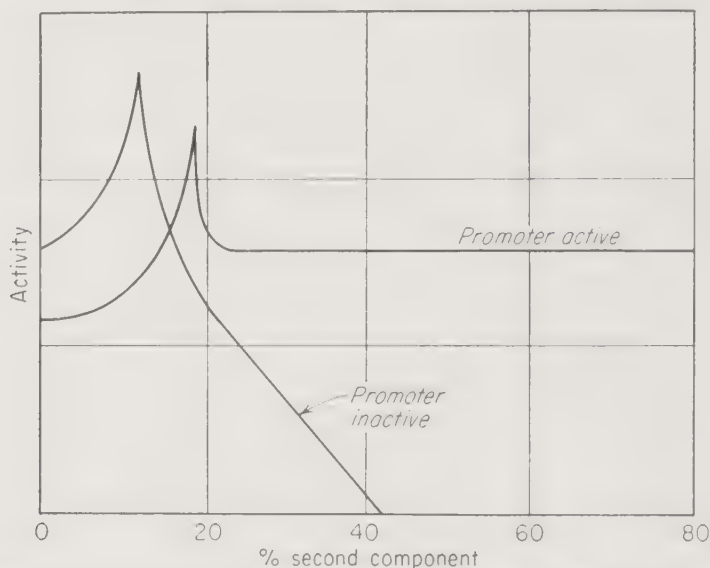


FIG 11-6. Effect of promoter on catalyst activity. (From R. H. Griffith, *The Mechanism of "Contact Catalysis,"* 2d ed., Oxford University Press, New York, 1946.)

lowered its activity by over 90 per cent. When this poison is firmly attached to the catalyst, it is a *permanent poison*. In some cases the poison is easily displaced, and it is then termed a *temporary poison*. A temporary poisoning effect is produced by water vapor on an iron-alumina-potassium oxide catalyst¹² as shown in Fig. 11-7. Here 0.32 per cent water vapor was introduced in the synthesis-gas mixture being fed to an ammonia reactor. The poisoning effect of this water vapor caused a rapid reduction in the per cent ammonia in the gases leaving the reactor. The water vapor was shut off after 60 min, and the catalyst rapidly returned to normal. If hydrogen sulfide had been added instead of water vapor, the activity of the catalyst would have been permanently impaired. Another type of poisoning is that produced by one of the by-products of the reaction such as carbon in reactions of acetylene in the presence of zinc catalysts. The effects of this type of poison may be minimized by

¹² P. H. Emmett and S. Brunauer, Jr., *J. ACS*, **52**:2682 (1930).

proper design of the reaction unit to avoid the accumulation of the retarder.

Catalytic activity is a surface action occurring at the solid-gas interface; thus the interior of the solid need not have catalytic activity. The catalyst may be impregnated on an inert material which then serves as a carrier. If the carrier is well mixed with the catalyst, it can act as a diluent and reduce the activity. When the catalyst is localized on the surface of the carrier, rather large percentages of the latter may be used before the activity is adversely affected. A suitable carrier may aid in

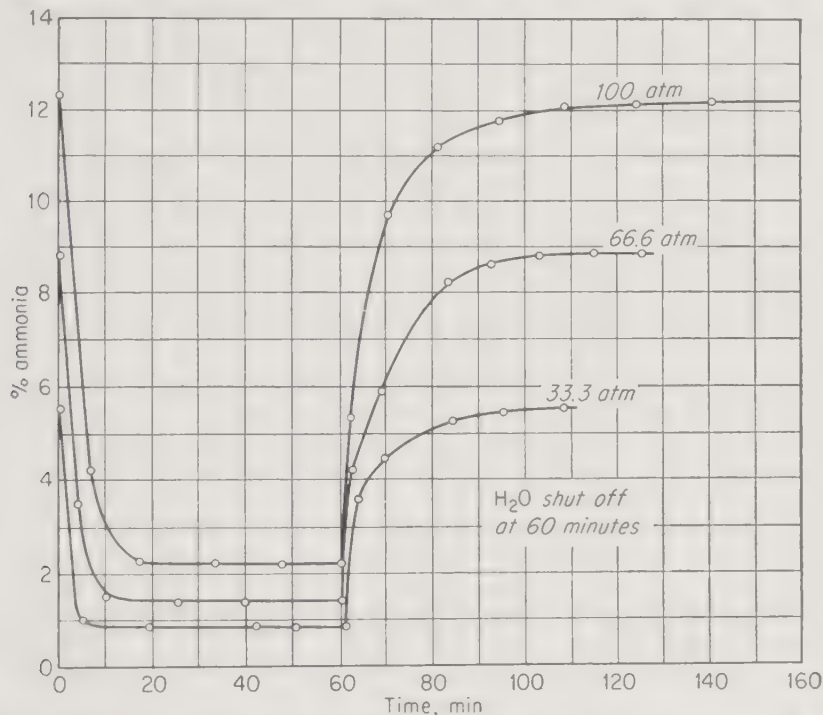


FIG. 11-7. Temporary poisoning of a catalyst. [From P. H. Emmett and S. Brunauer, *JACS*, **52**:2682 (1930).]

preserving activity at temperatures higher than would be possible with the catalyst alone. Physical changes in the catalyst or sintering of the surface with consequent reduction in the number of active centers is inhibited by this means.

A chemical reaction may take place in contact with a catalyst in a batch-type process with the reactants exposed to the catalyst for a given period of time and then withdrawn. The reaction may also be carried out as a flow process with the reaction mixture flowing continuously over the catalyst surface or through a bed of the catalyst in the form of particles or pellets. The latter method is commonly used in large-scale industrial reactions. The reaction time or time of contact with the catalyst in the flow process depends on the volume of the catalyst chamber and

the volume rate of flow of the gases. The *space velocity* is defined as the ratio of the volume of the reactant mixture (measured at standard temperature and pressure) which passes through the catalyst bed per hour, to the volume of the bed. According to this definition, the units of space velocity are hr^{-1} . For a given bed and reaction temperature and pressure, the space velocity is a measure of the reciprocal of the total reaction time. The *conversion* may be expressed as the weight of product formed per unit volume of reaction mixture. The *space-time yield* is the weight of product formed per hour per unit volume of catalyst bed. The space-time yield is the product of space velocity and the weight of product formed per unit volume of reaction mixture. As the space velocity is increased from a low value, the conversion is not at first affected to any marked extent and the space-time yield increases in proportion to the space velocity. At higher space velocities, the conversion may decrease considerably, causing the space-time yield to be less than proportional to the space velocity. A point is finally reached where further increase in space velocity cannot be justified by the increase in space-time yield obtained. The most economical operation will usually be found at an intermediate space velocity with a conversion somewhat less than that at equilibrium (low space velocity).

In many reactions, and especially those producing organic compounds, a number of products may be formed. A given catalyst then acts selectively in favoring the formation of a single product. *Specific action* by the catalyst is increased by the proper selection of reaction conditions. Thus the number of compounds which can be formed from carbon monoxide and hydrogen is legion. Methane is produced at atmospheric pressure and 380°C over a nickel catalyst. Higher-molecular-weight paraffin hydrocarbons are produced at atmospheric pressure and temperatures as low as 180°C with a cobalt-thoria catalyst as in the Fischer-Tropsch process. These hydrocarbons are isomerized to branched hydrocarbons with higher octane numbers at pressures of 300 atm and 450°C over thoria-alumina or zinc oxide-alumina catalysts. Zinc oxide-chromium oxide or zinc oxide-copper oxide catalyst at 300 atm and 300 to 350°C yields methanol, while higher temperatures cause the reaction to proceed to the formation of higher alcohols (excepting ethanol).¹³

It is not as yet possible to predict with assurance what catalyst should be used for a new and untried reaction. Experience has, however, shown that certain catalysts are usually effective for specific types of reactions. Chapter 2 includes a number of characteristic high-pressure reactions with the catalysts known to be effective in each case.

Preparation of Catalysts. The development or improvement of many industrial processes involves the selection or improvement of a catalyst.

¹³ P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, **22**:1051 (1930).

This includes selection of the catalyst elements or compounds and preparation of these in the most effective physical form. A catalyst suitable for a laboratory reaction may not be suitable for reactions on an industrial scale. The cost of the ingredients and the cost of preparation are likely to be a more serious factor in the latter case. The dimensions of the reactor may emphasize the problems of heat removal, transfer of reactants and products to and from the catalyst, pressure drop due to flow through the catalyst bed, life of the catalyst, and ease of regeneration. The cost of removing traces of catalyst poisons from technical-grade reactants often dictates the use of catalysts which are less active but have greater resistance to these poisons. For example, elemental metal catalysts are well known to be highly sensitive to such poisons as halogen and sulfur compounds present in technical-grade materials. Oxide catalysts, on the other hand, are more tolerant of these impurities.¹⁴

The development of a catalyst consists of trial-and-error procedures, but extensive past experience now can be called upon to limit the trials. A typical catalyst development for a specified reaction might consist of the following steps:

1. Choose from Chap. 2 or more extensive tabulations¹⁵ the single elements or compounds known to be effective in reactions of the type specified. By actual test, select those that are promising.
2. Test *mixtures* of those materials selected in step 1.
3. Improve the efficiency of the materials selected in steps 1 and 2 by *increasing the ratio of effective surface to volume*. This may be done by varying the method of preparation to give different physical forms of the activated catalyst. The selected compounds may be spread on the surface of, mixed with, or impregnated in, suitable inert carriers or supports. The surface is more likely to be active if prepared as one chemical compound and then changed to another of different density and crystal structure after being put in place. This is known as *activation* of the catalyst. Thus an iron catalyst may be prepared as an oxide or mixture of oxides and reduced to the elemental state in the reactor. A nitrate may be decomposed to the oxide or the element. The catalyst is then apt to be porous and to contain extensive internal active surface which it would not have if prepared initially in its final chemical form as a dense particle.
4. Add small amounts of one or more other compounds during the preparation to serve as promoters, and select the most effective combinations.
5. Vary the size of the catalyst particles.

¹⁴ H. S. Taylor, p. 587, "Chemical Engineers' Handbook," 2d ed., J. H. Perry, editor, McGraw-Hill Book Company, Inc., New York, 1941.

¹⁵ S. Berkman, J. C. Morrell, and G. Egloff, "Catalysis," Reinhold Publishing Corporation, New York, 1940.

6. The best selections from the above trials should then be subjected to extensive tests under actual process conditions to compare their life and ease of regeneration.

7. The feasibility of modifying the process for preparing the reactants and the consequent effect on the order of preference of the catalysts under test should be explored.

A number of measurements have been devised to aid in understanding the detailed form and structure of catalysts. These measurements should be correlated with catalyst performance. Such measurements include X-ray diffraction, electron micrographs, magnetic susceptibility, particle size, total surface area, porosity, pore-size distribution and the like. Hougen¹⁶ cites numerous references concerned with measurements made on catalysts.

11-3. Types of Reactors. Chemical reactions take place in many locations under numerous combinations of conditions. Each of these situations might be included in a list of reactors. The types described here will be representative only and have been selected as the ones most likely to have applications in high-pressure industrial operations.

A classification of reactors which depends on broad principles of similarity is suggested by Caddell and Hurt.¹⁷ This classification considers the reacting phases from the standpoint of the reactants and catalysts but not the products, as shown in Table 11-1.

TABLE 11-1. CLASSIFICATION OF REACTORS

<i>Homogeneous</i>	<i>Heterogeneous</i>	
Gas phase	Gas-solid phases	Liquid-liquid phases
Liquid phase	Gas-liquid phases	Solid-solid phases
Solid phase	Liquid-solid phases	Gas-solid-liquid phases

Homogeneous reactors include the batch reactor, the pipeline-type reactor, the single constant-composition reactor, and a series of constant-composition reactors. In the *batch reactor* (or kettle) the reactants and catalyst form a single phase and are charged to a vessel and agitated for a period of time. If the temperature is constant, the rate of reaction is usually greatest at the start and decreases as the reactants are depleted from the vessel and the concentration of products increases. The mixture containing the products is removed from the reactor at the end of the reaction period. The reaction reaches a given fraction of the equilibrium conversion during this time, and the rate of reaction is the lowest at the end of the period of any time during the period.

¹⁶ O. A. Hougen, Reaction Kinetics in Chemical Engineering, *Chem. Eng. Progr. Monograph Ser.*, **47**(1):34-40 (1951).

¹⁷ J. R. Caddell and D. M. Hurt, *Chem. Eng. Progr.*, **47**:333 (1951).

Essentially the same conditions are provided by a *continuous-flow pipeline-type reactor*. This term "is used to designate any flow system in which: (a) reactants are fed at one end of a reactor having a large effective length to diameter ratio and react under conditions of varying composition (changing reaction environment) along the length of the reactor, and (b) the mixture containing the products is withdrawn at the opposite end. In such equipment, the reaction proceeds kinetically in the same way as in a batch kettle."¹⁷

In the third type, reactants are fed continuously to a single stirred vessel and the mixture containing the products is removed continuously. When the stirring is adequate to maintain uniform composition in the

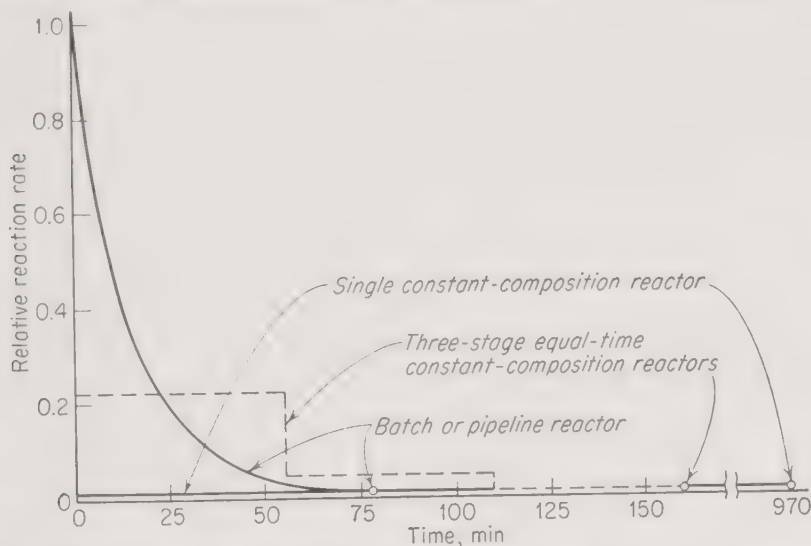


FIG. 11-8. Variation of reaction rate with time (also with distance in a flow reactor) in homogeneous-batch reactors.

vessel, the composition of the product stream is the same as that in the vessel, and the reaction takes place at this constant composition. Since this is the final composition, the rate is a minimum and considerably lower than the average rate in a batch reaction. To increase the rate of reaction during the formation of part of the product, a series of, say, three constant-composition reactors may be used. The stream leaving each of the first two reactors contains a lower concentration of product, and the rates of reaction in these are greater than in the last kettle in the series. The total reaction time (or volume of the three reactors) will be larger than for the batch reactor. The variation in reaction rate with these types is shown in Fig. 11-8. The curved line represents a typical variation in rate of reaction, relative to an initial rate of unity, vs. time in a batch (nonflow) reactor or vs. distance in a pipeline (flow) reactor. The area under the curve is proportional to the fractional conversion accomplished in the reactor. This area must be the same to attain the same

fractional conversion in different types of reactors. For a single-stage constant-composition reactor, the rate of reaction is the final rate in the batch reactor, and the time for the same fractional conversion is much longer in order to provide the same area. The three stages of equal-time (equal-volume) constant-composition reactors are shown by the three step dashed line. This requires a shorter time than the single stage. Temperature control is accomplished with these reactors by using internal coils or external jackets.

Heterogeneous reactions are frequently carried out in fixed beds of catalyst. Arrangements for this type of reactor will be described in the following paragraphs. If the heterogeneous mixture is in the form of a stable suspension, emulsion, or fluidized bed, one or more of the reactors described for homogeneous reactions may be used. When the catalyst is in pellets or aggregates, it is placed in a layer or bed and the reactants flow through the bed. The control of the temperature throughout the reactor should be considered in the design. Of major concern is the proper balancing of heat transfer within the catalyst bed to maintain the reaction at a rate which is balanced with the rest of the process and which will avoid localized overheating of the catalyst and loss of catalyst activity. A few degrees variation in the catalyst temperature may have a significant effect on the rate of reaction and on the rest of the system. The control of temperature will be discussed in a later section.

11-4. Principles of Design. Designing, constructing, and operating a satisfactory high-pressure reactor have several aspects as follows:

1. Choice of materials of construction and design to avoid chemical attack
2. Stress analysis of the steel or alloy vessel
3. Arrangements for heat transfer to control the temperature in the catalyst bed and protect the materials of construction
4. The specification of the size or volume of the reactor space to provide the fractional conversion expected
5. The design of closures and fabrication procedure

In addition, a choice must be made of a suitable catalyst and its method of preparation. The preparation of the reactants and their purity will influence the design of the reactor. The decision as to many of the specifications must be based on the economics of the process, and a number of possible designs should be considered in order to ensure the lowest cost of the product.

The high pressures employed in large-diameter vessels used for commercial production require thick walls of high strength steel. The steel walls will, in general, have considerably greater strength if they are not subjected to the temperatures encountered in the catalyst bed. A saving in cost can be made by so designing the reactor that the temperature of

the region next to the pressure-retaining steel wall is less than the temperature in the interior of the reactor. This results in a temperature gradient inside the reactor. Such gradients are also frequently present in the steel walls themselves. The calculation of stresses in thick-walled cylinders, both with and without thermal gradients, is discussed in Chap. 6. The stresses existing in special shapes of vessels and localized near fittings required for the introduction and removal of reactants and products are not so easily subject to mathematical analysis. Design of such parts depends on more empirical methods verified by adequate tests to failure.

In the earlier design of reaction vessels, the steel walls were subjected to the action of hydrogen, nitrogen, and other gases at temperatures ranging from 200 to 400°C and higher. Ordinary high-carbon steels are readily attacked by hydrogen under these conditions, the hydrogen reacting with the carbon in the steel and resulting in a weakened and porous wall. This situation at first led to the use of special alloys which contained chromium, tungsten, vanadium, nickel, and manganese. In recent years the problem has been handled by changing the reactor design so that the wall of the reaction vessel is not subjected to temperatures much in excess of 100°C. Medium-carbon steel has shown no evidence of attack when subjected to a hydrogen-nitrogen mixture at 800 atm and 200°C for 10 to 15 years. These features of the reactor design¹⁸ are shown in Fig. 11-9. This figure is a cross section through an ammonia-synthesis reactor. The stresses due to the high internal pressures occur in the thick, laminated converter shell. This shell is protected from contact with the reactant gases by a thin liner of suitably resistant alloy. It is insulated from the high temperatures that occur in the reaction space by a layer of insulation inside the catalyst-basket shell. Heat transferred through this insulation and the catalyst-basket shell is absorbed by the relatively cool incoming gas and is swept back into the reactor.

Material and Heat Balances. Chemical reactors are either of the batch type, in which conditions change continuously with time, or of the steady-state-flow type, in which conditions at each position in the reactor do not change with time. In the latter case conditions at each position may change slowly because of a decrease in the activity of the catalyst. Steady-state reactors, with variations from one position to another, are the rule in high-pressure processes. The quantitative treatment of the reactor includes material and heat balances. In order to allow for the variations from one position to another the balances should be made initially on a small, differential, part of the total volume and then integrated to include the total volume of the reactor. The volume is

¹⁸ A. V. Slack, H. Y. Allgood, and Harold E. Maune, *Chem. Eng. Progr.*, **49**:393 (1953).

chosen small enough so that at any instant the temperature and concentration are uniform within it. When the patterns of changing temperature and concentration in the reactor at any instant are complex, differential equations are used to arrive at equations which take these variations

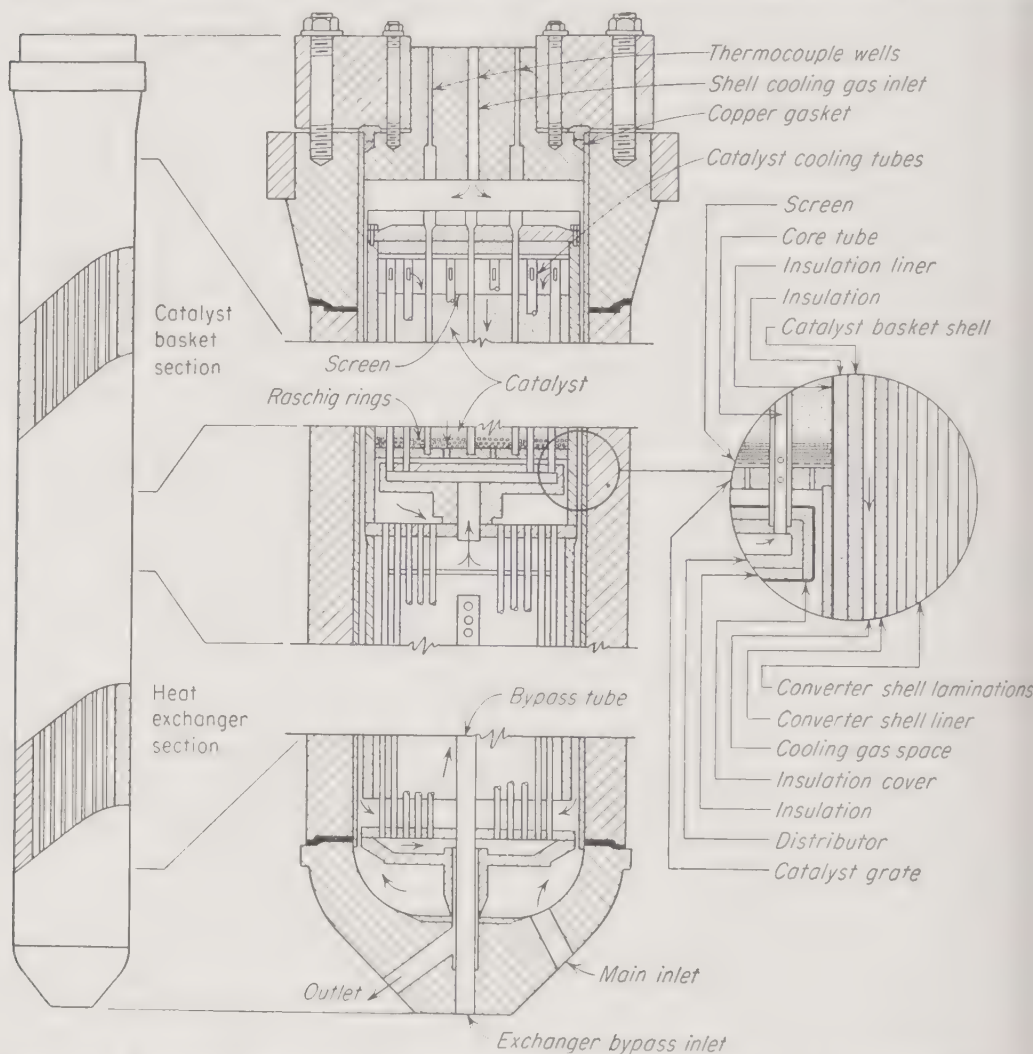


FIG. 11-9. Internal arrangement of reactor for synthesis of ammonia at high pressure. [From A. V. Slack, H. Y. Allgood, and H. E. Maune, *Chem. Eng. Progr.*, **49**:393 (1953).]

into account. These equations result from the heat and material balances, and to determine the changes through the whole reactor they must be integrated either analytically, graphically, or numerically. When composition and temperature are uniform throughout the reactor and do not change with time as in the constant-composition-type reactor, integration is not required since the balances may be based on the volume of the whole reactor. This type of reactor is treated with a much simpler mathematical analysis.

The most general analysis for an incompressible fluid is described by Baron¹⁹ and is based on a modification of the Fourier-Poisson differential equations. These are concisely expressed in terms of vector notation as follows:

$$\frac{\partial(c_p \rho t)}{\partial \tau} = - \operatorname{div} (-k \operatorname{grad} t) - \operatorname{div} c_p \mathbf{G} t + R_i \lambda M_i$$

$i = \text{key component} \quad (11-19)$

and
$$\frac{\partial c_i}{\partial \tau} = - \operatorname{div} (-D_i \operatorname{grad} c_i) - \operatorname{div} \mathbf{V} c_i - \frac{R_i M_i}{\rho_i}$$

$i = 1, 2, \dots, n \quad (11-20)$

A complete explanation of this notation is outside the scope of this book, but a qualitative explanation will be given. The reader is referred to texts on advanced mathematics²⁰ and fluid mechanics²¹ for further information. The equations take account of the movement of heat and matter into and out of a small differential volume and relate these to the accumulation or depletion and the generation of these entities within the volume. Heat may be generated by a chemical reaction, and at the same time the reaction generates the products of the reaction and consumes the reactants. The equations consider movements in three dimensions and include the mass velocity \mathbf{G} and the linear velocity \mathbf{V} as vectors in order to indicate both their direction and magnitude. The boldface symbol designates a vector quantity. All other quantities in the equation are indicated by a magnitude only and do not have a direction. These are scalar quantities.

Equation (11-19) is a heat balance on a differential volume dV of the reactor shown pictorially in Fig. 11-10. The term on the left of the equation represents the rate of change of sensible heat in this volume. The sensible heat in the differential volume changes as the result of the net rate of heat transported in and out by thermal conduction and the net rate of heat transported by the flow of fluid into and out of the volume in the three coordinate directions. These rates are given by the first two terms on the right and are represented in Fig. 11-10. Heat may be generated within the volume, and the net rate of generation is given by the last term on the right. The reaction involves n chemical species of reactants, products, and inerts. Equation (11-20) is derived from n material balances on the differential volume, one for each of the n species. The rates of transport of component i are represented in Fig. 11-10. The

¹⁹ Thomas Baron, *Chem. Eng. Progr.*, **48**:118-124 (1952).

²⁰ I. S. Sokolnikoff and E. S. Sokolnikoff, "Higher Mathematics for Engineers and Physicists," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

²¹ L. M. Milne-Thompson, "Theoretical Hydrodynamics," 2d ed., The Macmillan Company, New York, 1950.

term on the left in the equation is the rate of change of the i th molecular species within the volume, and this is equal to the sum of the three terms on the right representing, respectively, the net rate of diffusion of component i into the volume, the net rate of transport of component i by flow into the volume, and its net rate of increase or decrease due to the chemical reaction within the volume. These equations account for the change

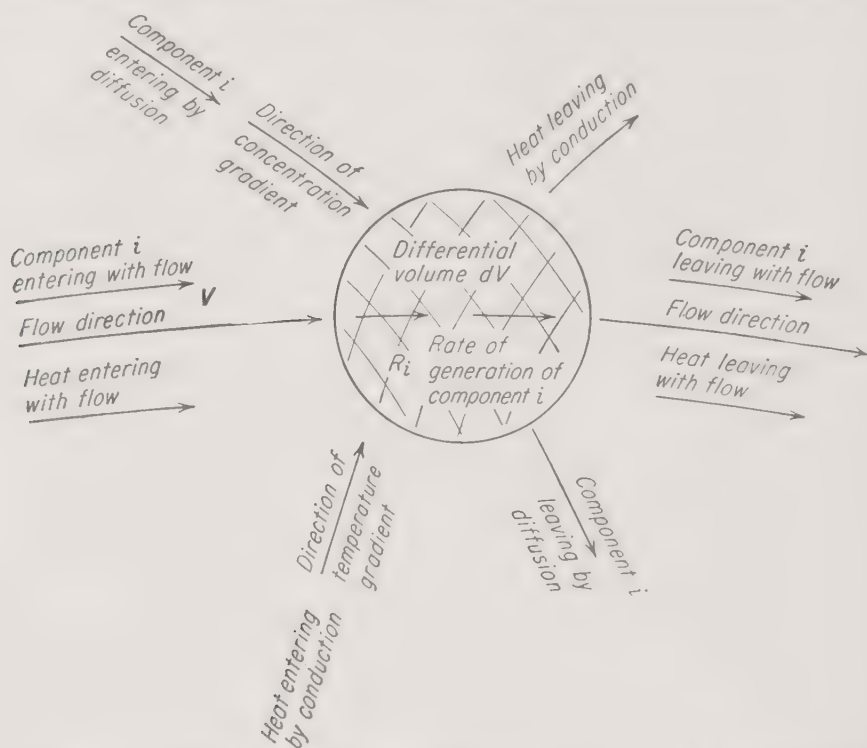


FIG. 11-10. The movement of heat and matter into and out of a differential volume dV in a chemical reactor.

in temperature, concentration, velocity, and rate of reaction in the three coordinate directions and with time. Variation of all these quantities is normally not encountered in any one reactor, and the analysis of each special case can be simplified accordingly.

In a *homogeneous batch reactor*, temperature and concentration are maintained uniform throughout the vessel by agitation, and only variation in the rate of reaction with time need be considered. A material balance around a unit mass of material in the reactor is expressed by²²

$$\frac{dy_i}{d\tau} = R_i V_c M_{av} \quad (11-21)$$

or

$$R_i = \frac{dy_i}{M_{av} V_c d\tau}$$

²² O. A. Hougen and K. M. Watson, "Chemical Process Principles," pt. 3, p. 822. John Wiley & Sons, Inc., New York, 1947.

The time required for a selected conversion y_{i2} may be obtained by evaluating the integral

$$\tau = \int_{y_{i1}}^{y_{i2}} \frac{dy_i}{V_r R_i M_{av}} \quad (11-22)$$

In a steady-state-flow system (e.g., pipeline-type reactor) without mixing in the direction of flow, a material balance may be based on an element of reactor volume dV_r . All variations in temperature and concentration are neglected except those in the direction of flow, and it is assumed that heat and mass are transported in this direction only by the flow of the fluid. The resulting equation does not involve time as a variable. It is

$$R_i dV_r = \mathfrak{F} dy_i \quad (11-23)$$

This equation is integrated to obtain the reactor volume according to

$$\frac{V_r}{\mathfrak{F}} = \int_{y_{i1}}^{y_{i2}} \frac{dy_i}{R_i} \quad (11-24)$$

Equations (11-23) and (11-24) have been integrated for several cases and the results tabulated by Hougen and Watson.²²

Temperature Control. The temperature within a reactor may be controlled by the addition of heat from an external source or by the removal of heat from the reactor. Agitated or fluidized reactors may be maintained at a predetermined temperature, or the temperature in a batch reactor may be varied according to a specified cycle. This temperature control requires well-designed heat-transfer surfaces, usually in the form of internal coils or an external jacket. The reaction may be isothermal (constant temperature) or adiabatic (no heat exchange with an external source or heat reservoir). In a reactor containing a bed of catalyst, the situation is more complex.

As an example, consider the synthesis of ammonia. The reaction of a 3:1 molar hydrogen-nitrogen mixture liberates 22,400 Btu/lb mole of ammonia formed. If this heat is used adiabatically to raise the temperature of the ammonia formed together with the unreacted nitrogen and hydrogen, the mixture would attain a higher and higher temperature as the per cent conversion increases. The final adiabatic temperature is shown, by the curves marked t_0 in Fig. 11-11, as a function of the per cent ammonia in the reaction mixture for several temperatures of the original hydrogen-nitrogen mixture before reaction and at three pressures. The other curves show the per cent ammonia at equilibrium. At low per cent conversion, and especially when starting the reaction, it is necessary to add heat to bring the gases to the reaction temperature and to replace heat lost through the walls of the converter. As the per cent conversion increases beyond the point where the heat of reaction is just sufficient to

replace heat losses, it may be necessary to remove the excess heat of reaction by suitable heat-exchange surface incorporated in the catalyst bed, or the temperature may rise higher than is desirable. A more complete discussion of the temperature-heat of reaction relationship will follow in the next section. At the higher pressures, this heat release occurs in a smaller volume, and a greater rate of heat transfer per unit volume of catalyst is required. The heat release does not occur uniformly throughout the catalyst bed but parallels the rate of reaction as it varies from one

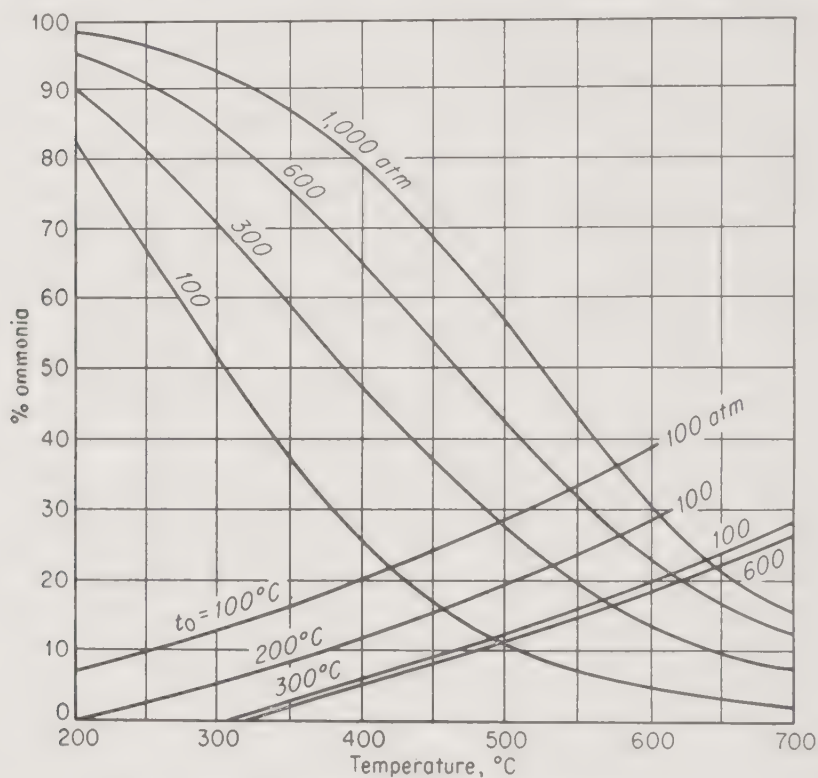


FIG. 11-11. The adiabatic reaction temperature.

region of the bed to another. For a catalyst bed of uniform activity and at essentially constant pressure, the rate of reaction will depend on the local temperature of the catalyst and the per cent ammonia in the gases at that point. At a fixed temperature, the rate of formation of ammonia is highest when the per cent of ammonia is low. This rate decreases as the reaction proceeds and more ammonia is present in the gases. There is a tendency for localized high temperature, or hot spots, especially where the new gas enters the catalyst bed. These hot spots cause a decrease in the activity of the catalyst. An ideal reactor design incorporates a greater ratio of heat-transfer surface to catalyst volume near the entrance to the bed and also provides increasingly greater contact time between the gases and the catalyst at somewhat lower temperatures as the reaction

progresses in passing through the bed. The aim should be to hold back the reaction near the entrance to the extent that the heat of formation can be dissipated from the catalyst surface to the gas and adjacent heat-transfer surface. The reaction should then be encouraged to take place as rapidly as possible after the ammonia concentration begins to build up so as to approach the limiting equilibrium concentration. Practical arrangements for fabrication and progressive changes in the bed limit the extent to which the ideal design may be attained.

From a practical viewpoint, the more simple the design can be made for fabrication and maintenance purposes the better. Good design requires adequate heat-exchange surface within the catalyst bed to control the temperature rise of the gases resulting from the liberation of the heat of reaction. Sufficient surface outside the bed should be provided to pre-heat the reaction gases and cool the product gases by interchange of heat between these two streams. Both gas streams thus enter and leave the reactor at temperatures well below that at which the reaction takes place. A "cold shot" connection for introducing cold gas directly to the exchange surface within the bed is also desirable for temperature control. Maximum utilization of the converter volume is to be sought because the production capacity and operating life of the reactor are proportional to the catalyst volume. The best design is usually a compromise between the ideal and the practical.

Several arrangements of the heat-transfer surface within the catalyst bed have been used. Typical arrangements are given in the following list and are shown in Fig. 11-12.

1. External heat exchanger
2. Exchange between concentric annuli
3. Catalyst in tubes, cooling gases outside
4. Cooling gas inside tubes passing through catalyst bed
 - a. Tubes make single pass through bed
 - b. Tubes make double pass through bed with return bend
 - c. Thimble type with gases passing through a central inner tube and back through an annular space between tube and thimble

A complete reactor with the cooling gas inside tubes is shown in Fig. 11-9. When using a heat exchanger external to the bed, the bed is divided into layers and the gas is cooled by a heat-transfer arrangement between the beds. In the other arrangements shown, heat is removed directly from the gases while in contact with the catalyst. The reacting gas then flows through the bed in one direction, and heat flows in a direction at right angles to the direction of the gas flow and toward a heat-transfer surface.

Autothermal Processes. Frequently, the heat of an exothermic reaction is used to raise the temperature of the reactants from an initial temperature T_0 to the temperature at the entrance to the reactor. No external

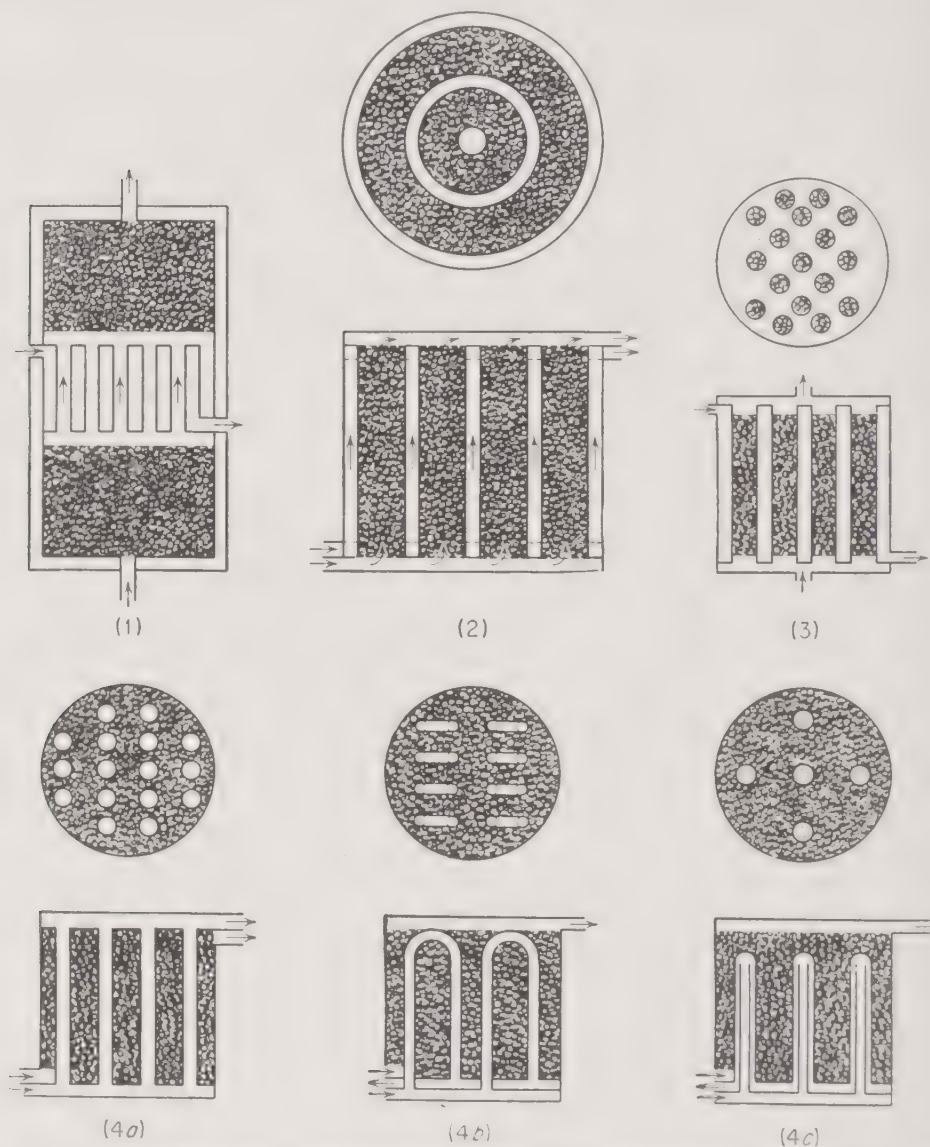


FIG. 11-12. Arrangement of heat-transfer surface in a catalyst-bed reactor. 1. Separate heat exchanger. 2. Concentric annuli. 3. Catalyst in tubes—coolant outside. 4. Fluid coolant in tubes—catalyst outside. (a) Tubes make single pass. (b) Tubes make two passes. (c) Tube-and-thimble type.

heat source is required although heat may be exchanged within the reactor. This arrangement is termed an *autothermal process*²³ and is important in the design of many high-pressure reactors. A discussion of this method of temperature control will aid in understanding the character-

²³ C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).

istics of this type of process such as the necessity for ignition by external heating to reach steady-state operation, the requirement for a variable heat-transfer efficiency to allow for a variable catalyst activity, and the use of a variable heat-transfer efficiency (or heat-transfer area) to obtain a maximum yield of product from the converter.

A simple case of an autothermic reaction is described by van Heerden and is treated in this chapter. The quantitative application to the ammonia-synthesis reactor is included in Chap. 12. Consider an agitated constant-composition reactor of fixed volume, and therefore constant residence time, with the reactants entering continuously at the temperature T_0 and reacting at the constant temperature T_r in the reactor. The products continuously leave the reactor at the temperature T_r . This process is shown in Fig. 11-13. The heat of reaction raises the temperature of the

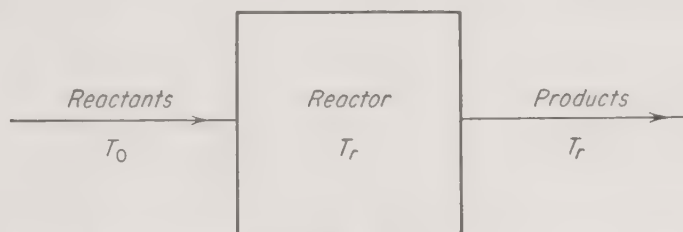


Fig. 11-13. A simple autothermal process. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

reactants from the temperature T_0 to the reaction temperature T_r . To simplify the discussion, consider the case where the heat capacity of the reactants is the same as that of the products and is independent of temperature. Let C be the heat capacity of the reactants or products per pound mole of one of the reactants (the key reactant). Let Q_r be the heat generated per pound mole of the key reactant by that part of the complete reaction that has taken place at the fractional conversion accomplished in the reactor. Then the increase in sensible heat of the reactor contents due to the reaction is

$$Q_c = C(T_r - T_0) \quad (11-25)$$

In reality, $Q_c = Q_r$ at any per cent conversion to satisfy the heat balance, but imagine for the moment that Q_c and Q_r are determined independently by the reaction temperature.

At a constant feed rate and essentially fixed residence time in the reactor, the heat Q_r produced by the reaction will depend on the reaction temperature in the manner shown in Fig. 11-14. At low reactor temperatures, the reaction will be so slow that the fractional conversion and Q_r are practically zero. At a certain temperature level, the reaction rate starts rising rapidly with temperature, and the fractional conversion then increases rapidly with increase in T_r . When not limited by an equilib-

rium conversion, the reaction will go to completion as a result of a rather small increase in the reactor temperature. When the temperature of complete conversion is reached, no further rise in Q_r will take place with an increase in the reaction temperature.

Q_c is represented by a straight line b since the sensible heat of the gas is linear in its temperature when the heat capacity is constant. This line intersects the temperature axis at T_0 , and it intersects the curve for Q_r at T_i and T_s . These three temperatures are the only conditions which satisfy the heat balance, $Q_r = Q_c$, for the steady-state process. T_0 is the temperature of the stable, nonreacting state, and T_s is the temperature of

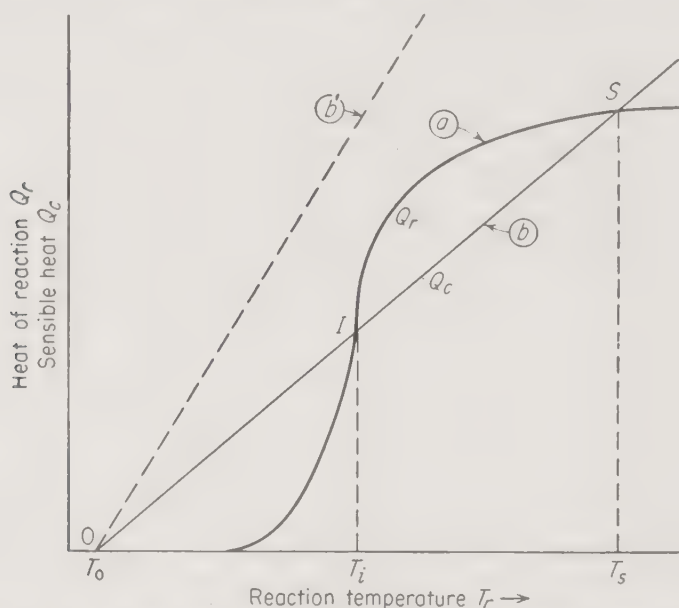


FIG. 11-14. Heat of reaction and sensible heat of mixture vs. reaction temperature [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

the stable, steady reacting state. The temperature T_i is the ignition temperature and represents an unstable condition. Starting at T_0 with no reaction, temperature T_i must be reached by supplying heat from an external source before the reaction can generate enough heat of reaction to attain the stable, steady reacting state at T_s . Operation at the temperature T_i is unstable since a slight drop in temperature would result in liberation of too little heat to maintain this temperature and consequently would cause a further decrease until T_0 is reached. A slight increase in temperature will result in the liberation of additional heat of reaction until the stable state at T_s is reached. If the reaction is too slow or the heat of reaction is too low relative to the heat capacity of the reactants and products, curves a and b may not intersect. This condition is shown by the curve b' . An autothermic reaction is then not possible for the simple reactor system considered.

The conditions at the steady reacting state for the type of reactor being considered are affected by variations in the feed rate of the reactants, the heat losses to the surroundings, dilution of the feed, provisions for exchange of heat between the product and feed streams, and the limiting of the fractional conversion by thermodynamic equilibrium. These effects will be discussed.

An increase in the *feed rate* results in a decreased residence time in the reactor and thus a smaller fractional conversion and lower value of Q_r . This means that curve *a* is shifted to the right. The upper limiting value of Q_r for complete reaction remains the same at higher feed rates as shown

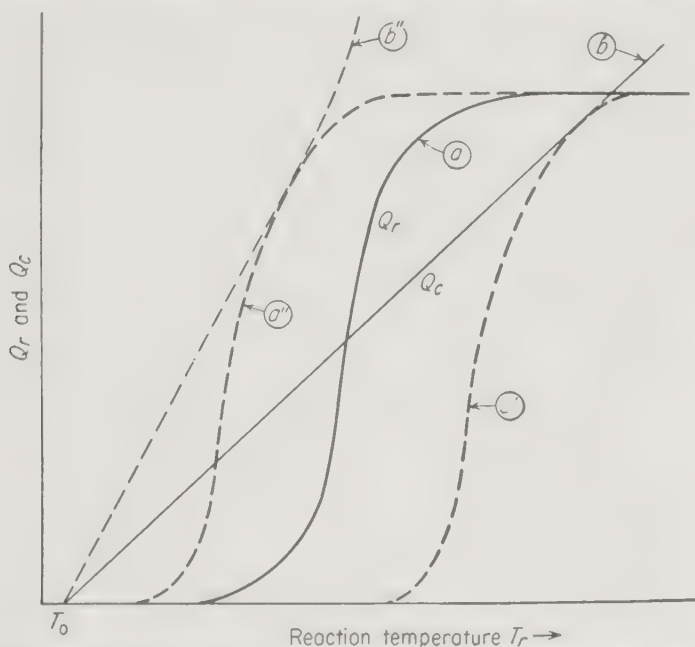


FIG. 11-15. Effect of variation in feed rate. [From C. van Heerden, *Ind. Eng. Chem.*, 45:1242 (1953).]

in Fig. 11-15. In the absence of heat losses to the surroundings, the slope of the straight line b is not affected by the feed rate. As the feed rate is further increased, curve a will ultimately reach the position a' . With any increase beyond this value, a stable, steady reacting state will no longer exist. Consequently, there is an upper limit for the feed rate of autothermic processes above which the reaction is extinguished.

The slope of the line b is equal to the heat capacity C . By definition, this is the heat required to raise the temperature of the reaction products from 1 lb mole of the key reactant one degree. Thus C increases when *dilutents* are added to the reactants or when part of the heat escapes as a *heat loss*. Larger values of C increase the slope of the line representing Q_c and may lead to the condition shown at b'' , where no stable reaction state exists. At low feed rates, the effect of an approximately constant heat

loss is especially pronounced, since this loss is a larger fraction of the heat generated and this sets a lower limit to the feed rate below which the reaction will be quenched. Heat losses are also greater at higher temperatures, and at low feed rates the line b'' becomes curved as shown in Fig. 11-15.

Heat may be recovered from the product stream by passing it through a heat exchanger with the incoming stream of reactants. This produces the opposite effect to that of a heat loss and thus reduces the value of C and the slope of the Q_c line. Heat recovery may be used to carry out a process autothermally, if this is impossible without heat recovery, and also to raise the steady-reaction temperature T_s . The recovery of heat

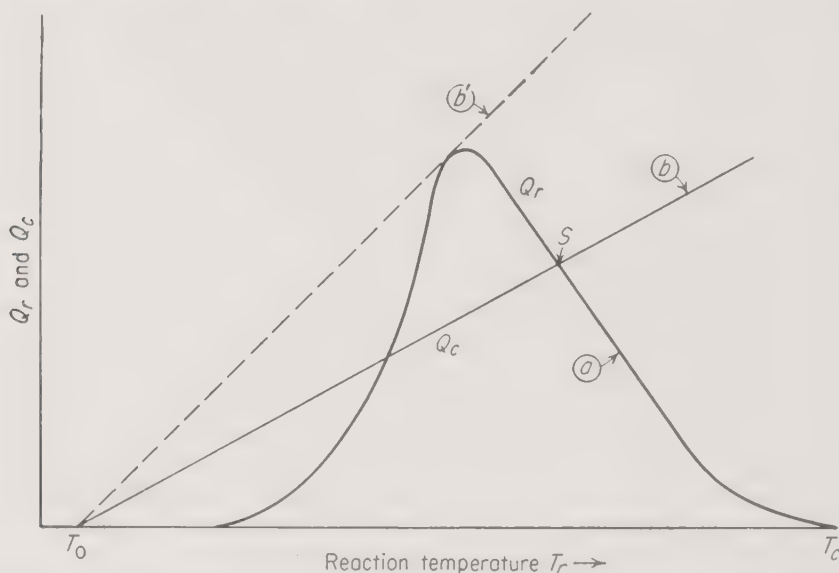


FIG. 11-16. Effect when equilibrium conversion decreases with increasing temperature. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

is necessary in some reactions such as the ammonia-synthesis reaction if the process is to be autothermal.

When chemical equilibrium between the reactants and products sets a limit to the fractional conversion attainable at a given reaction temperature, the Q_r curve in the diagram will have a different shape. At high temperatures where the fractional conversion is near equilibrium and the reaction does not go to completion, the heat produced by the partially complete reaction will be less. Thus, Q_r will reach a maximum at an intermediate temperature and will decrease with further increase in temperature. The steady reaction state thus lies on the decreasing part of the curve as shown in Fig. 11-16. A reduction in the slope of the Q_c curve increases the steady-reaction temperature and decreases the fractional conversion. Where this slope can be varied as by varying the amount of heat exchanged between product and reactant streams, it is useful to

choose as great a slope for the Q_c line as possible. This condition is shown at b' in Fig. 11-16. Under these conditions, which are at the limit of stable operation, the conversion will reach its maximum. The operating variables of a constant-composition steady-state autothermic reactor have been discussed. Application to a variable-composition steady-state-flow reactor operating autothermally will be described in Chap. 12.

Distribution of Temperature and Composition. The conditions throughout a catalyst-bed reactor may be calculated in some instances if the required information is available. A knowledge of the methods employed will be helpful in understanding operation of the reactor. The method requires the simultaneous integration of Eqs. (11-19) and (11-20). The method proposed by Baron¹⁹ will be described. Accurate calculations for an actual catalyst bed are apt to be tedious. A number of simplifications, however, lead to a method that is not excessively time-consuming. Only the case of a cylindrical reactor with flow in the axial direction will be considered, although the method is adaptable to other geometrical arrangements.

The following concepts are used as a basis.

- a.* Heat and mass are transported in the radial direction by the chance deflections of the stream by the catalyst pellets.
- b.* Transport by chance deflections in the axial direction is negligible compared to the ordinary transport by the fluid flowing in this direction.
- c.* Molecular diffusion is negligible compared to the transport by the fluctuations in the flow from the deflections caused by the pellets.
- d.* The change in total moles arising from the reaction to the extent that it takes place in the reactor is small.
- e.* There is no net flow in the radial direction. This does not preclude a variation in the radial direction of the bulk flow in the axial direction.

From *d* it can be shown that the reactants remain in the stoichiometric proportion they had on entering the reactor, and a single mass-balance equation will suffice to represent all components. A separate equation for each reactant and product in the mixture is not necessary. This single mass-balance equation can conveniently be expressed in terms of the fractional conversion \bar{f} of the limiting reactant. Equations (11-19) and (11-20) can now be converted to the form

$$\frac{\partial t}{\partial z'} = \frac{1}{N_{P'e}} \left[\frac{\partial^2 t}{\partial r'^2} + \frac{1}{r'} \frac{\partial t}{\partial r'} \right] + \frac{M_i Q_i \rho_B \lambda d}{c_p G_0} \quad (11-26)$$

$$\text{and} \quad \frac{\partial \bar{f}}{\partial z'} = \frac{1}{N_{P'e}} \left[\frac{\partial^2 \bar{f}}{\partial r'^2} + \frac{1}{r'} \frac{\partial \bar{f}}{\partial r'} \right] + \frac{Q_i \rho_B M_{nv} d}{G_0 y_1^0} \quad (11-27)$$

Reference should be made to Baron's original paper for further information on the steps involved in the derivation of Eqs. (11-26) and (11-27).

These differential equations may be put in the form of difference equations and made the basis of a graphical solution for the distribution of temperature and fractional conversion. The difference equations are

$$\Delta_z t = \frac{1}{N_{Pe}} \frac{\Delta z'}{(\Delta r')^2} \Delta_r^2 t + \frac{M_i \mathcal{R}_i \rho_B \lambda d}{c_p G_0} \Delta z' \quad (11-28)$$

$$\Delta_z f = \frac{1}{N_{Pe}} \frac{\Delta z'}{(\Delta r')^2} \Delta_r^2 f + \frac{\mathcal{R}_i \rho_B M_{av} d}{G_0 y_1^0} \Delta z' \quad (11-29)$$

Baron¹⁹ has developed a double stepwise simultaneous integration of these two equations by a graphical procedure. This incorporates the finite-difference methods developed by Nessi and Nissolle²⁴ and extends the method proposed by Grossman²⁵ for the integration of Eq. (11-28) to the simultaneous integration of Eqs. (11-28) and (11-29). This method is applied to the cylindrical tube of catalyst shown in Fig. 11-17. The tube is arbitrarily divided into a number of annuli, each with a radial thickness $\Delta r'$, and into a number of axial sections, each with a thickness $\Delta z'$. These are numbered as shown in the figure. The thickness $\Delta z'$ is determined by the relation

$$\Delta z' = \frac{1}{2} N_{Pe}' (\Delta r')^2 \quad (11-30)$$

A diagram is prepared as illustrated in Fig. 11-18. This consists of four quadrants. In quadrant II is plotted the temperature change due to the reaction during the time the fluid is flowing through the

axial distance $\Delta z'$ as a function of temperature at several constant values of fractional conversion. This temperature change is represented by

$$\frac{M_i \mathcal{R}_i \rho_B \lambda d}{c_p G_0} \Delta z'$$

²⁴ A. Nessi and L. Nissolle, "Méthodes graphiques pour l'étude des installations de chauffage et de réfrigération en régime discontinu," Dunod, Paris, 1929.

²⁵ L. M. Grossman, *Trans. Am. Inst. Chem. Engrs.*, **42**:535 (1946).

In quadrant III is plotted the change in fractional conversion during the time the fluid is flowing through the axial distance $\Delta z'$ as a function of

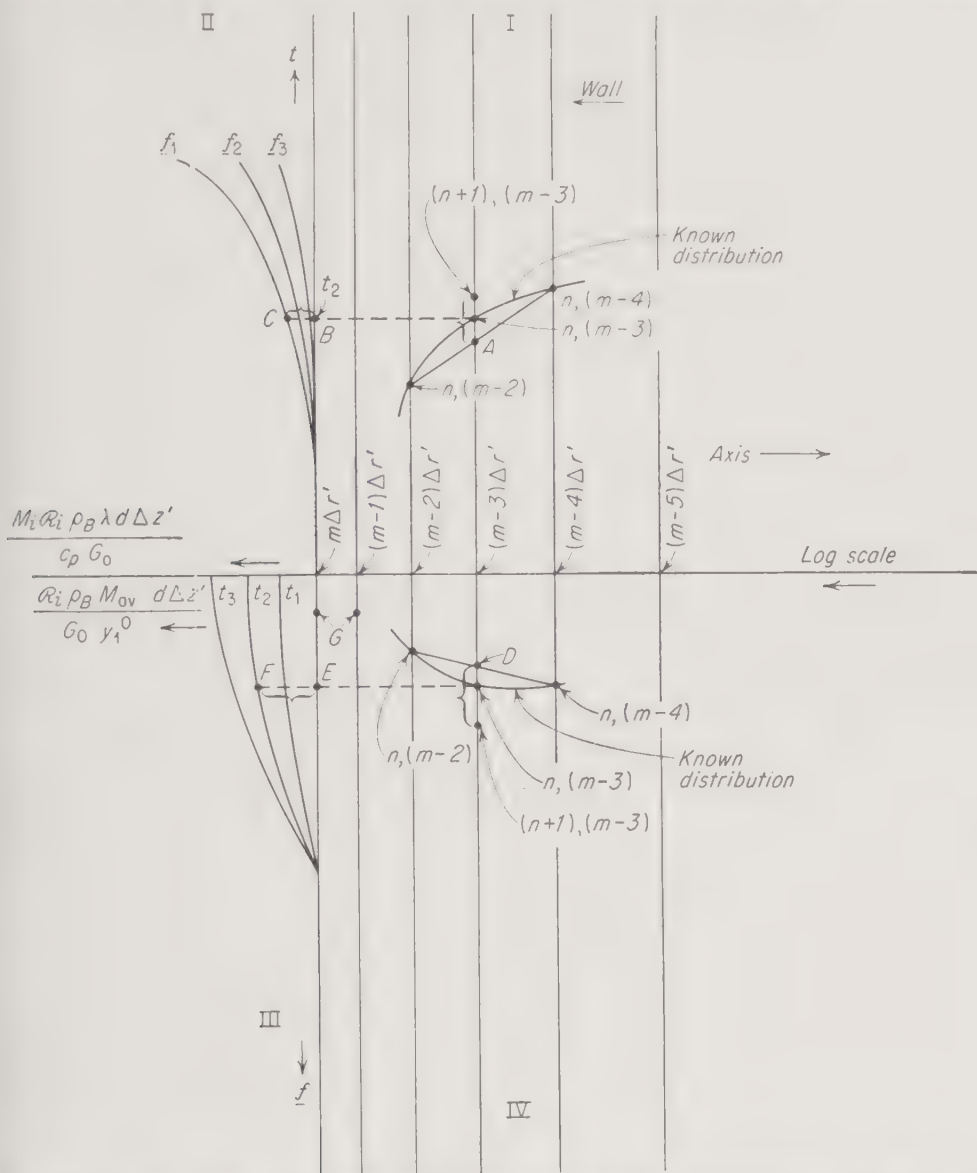


FIG. 11-18. Graphical calculation of temperature and concentration throughout a cylinder filled with catalyst. [From T. Baron, *Chem. Eng. Progr.*, **48**:118 (1952).]

fractional conversion at several constant values of temperature. This conversion is given by

$$\frac{R_i \rho_B M_{av} d}{G_0 y_1^0} \Delta z'$$

Radial distances are plotted from right (the reaction axis) to left (the reactor wall) on a logarithmic scale with a common abscissa between

quadrants I and IV. Temperature is plotted vertically upward on the common ordinate of quadrants I and II, and fractional conversion downward on the common ordinate between quadrants III and IV. Quadrant I is used to indicate the temperature variation with radial distance, and quadrant IV to indicate the variation in fractional conversion with radial distance. To start the calculation, the distribution of temperature and fractional conversion must be known at one section of the cylinder, say at z'_n . The stepwise graphical calculation then permits the determination of the distribution at successive sections $z'_n + \Delta z'$, $z'_n + 2\Delta z'$, etc. These cross sections will be denoted by the subscripts n , $n + 1$, $n + 2$, etc. The radial positions at successive increments of $\Delta r'$ will be denoted by the subscripts m , $m - 1$, $m - 2$, etc. Then the known distribution of temperature and fractional conversion are plotted in I and IV as shown.

The method of determining the temperature and fractional conversion at section $n + 1$, next to the one where the distribution is known, and at the radial position $m - 3$ will be illustrated. Repetition of this procedure at $m - 2$, $m - 1$, etc., across the section will yield the complete distribution at section $n + 1$. The same steps may be repeated for the next section, $n + 2$, and succeeding sections. The temperature at $n + 1$, $m - 3$ is obtained in three steps.

1. The temperatures at n , $m - 2$ and n , $m - 4$ on the known distribution curve are connected by a straight line to locate point A in quadrant I.

2. A horizontal line is drawn through the quadrant II at the fractional conversion at n , $m - 3$ on the known distribution curve. This locates points B and C .

3. The horizontal distance BC is added to A in a vertical direction to locate the desired temperature at $n + 1$, $m - 3$. This gives one point on the new temperature-distribution curve.

The fractional conversion is obtained by a similar procedure. In quadrant IV the fractional conversions at n , $m - 2$ and n , $m - 4$ on the known distribution curve are connected by a straight line to locate point D . A horizontal line is drawn through n , $m - 3$ on the known distribution curve to the line in quadrant III for the temperature at n , $m - 3$. This line locates points E and F . The horizontal distance EF is added vertically to D to locate the fractional conversion at $n + 1$, $m - 3$. This is a point on the new fractional-conversion distribution. Similar constructions are used to locate points at $n + 1$, $m - 2$; $n + 1$, $m - 4$, etc., to establish the temperature and fractional-conversion distribution at section $n + 1$.

Modifications of this construction may be used at the wall to allow for heat transferred through the wall.²⁶ The fractional conversion should

²⁶ M. Jakob, "Heat Transfer," vol. 1, chap. 20, John Wiley & Sons, Inc., New York, 1949.

not vary with the radius in the region near the wall. Such a variation would indicate a transfer of reaction components through the wall of the tube, which is not possible in the case under consideration. To avoid this anomalous result in the calculation, the fractional conversion at a radial distance $\Delta r'$ from the wall should always be set equal to that at the wall as shown at G in Fig. 11-18.

The construction described is applicable when the superficial mass velocity is uniform over the cross section of the cylinder. When this velocity varies with the radius, the plots in quadrants II and III should be based on the average mass velocity G_{av} . Then the distances BC and EF should be multiplied by $G_{av}/G_{r'}$ before these values are added to the points A and D . $G_{r'}$ is the mass velocity at the radius r' . Application of this method to a reactor for the synthesis of ammonia is described in Chap. 12.

11-5. Reaction Rate. The kinetics of the synthesis of ammonia on doubly promoted iron catalysts has been the subject of extensive investigations. This reaction is discussed in Chap. 12 and will serve as an example for a discussion of the factors which determine the rate of reaction in a catalytic reactor. Other reactions differ appreciably from this, but many of the underlying principles are similar.

NOMENCLATURE

- a Moles of reactant A, which reacts in stoichiometric proportion; b , moles of reactant B; r , moles of product R formed; etc..
- a Constant in Arrhenius equation
- c_i Concentration of component i , cu ft/cu ft; c_A , c_B , etc., moles per unit volume
- c_p Specific heat of mixture, Btu/(lb)(°F)
- C Heat capacity of the reactants and products per pound mole of the key reactant
- D_i Molecular diffusivity of molecular species i
- d Pellet diameter
- E Effective diffusivity, sq ft/hr
- F Free energy $H - TS$; $\Delta F^{\circ*}$, standard free-energy change for formation of the activated complex, Btu/lb mole
- \mathfrak{F} Feed rate, lb moles/hr
- f Fractional conversion of the limiting reactant
- G_0 Superficial mass velocity, lb/(sq ft)(hr); G_{av} , average mass velocity; $G_{r'}$, mass velocity at radius r'
- G Mass velocity expressed as a vector, lb/(hr)(sq ft)
- H Enthalpy, Btu/lb mole
- h Planck constant, 6.624×10^{-27} erg sec
- k Thermal conductivity, Btu/(hr)(ft)(°F)

- K Chemical-equilibrium constant; K^* , for formation of the activated complex from the reactants
 K_c Chemical-equilibrium constant based on concentration
 \mathcal{K} Boltzmann constant, 1.3805×10^{-16} erg/(molecule)(°K)
 k Reaction-rate constant
 M_{av} Average molecular weight
 M_i Molecular weight of compound i
 n moles of mixture
 \mathcal{N} Avogadro's number $6.02283 \pm 0.0022 \times 10^{23}$ molecules/g mole
 N_A Moles of component A in mixture; N_B , moles of B; etc.
 p Pressure, atm
 N'_{Pe} Modified Peclet number $= \left(\frac{\mu}{\rho E} \right) \left(\frac{dG_0}{\mu} \right) = N'_{Sc} N'_{Re}$
 Q Activation energy in Arrhenius equation
 Q_r Heat of reaction at a given fractional conversion per pound mole of the key reactant
 Q_c Sensible heat of reactants and products per pound mole of the key reactant
 R Gas-law constant
 R_i Rate of reaction, lb moles of compound i /(hr)(pound of catalyst) or
 R_i Rate of reaction, lb moles of compound i /(hr)(cu ft of reactor)
 r Distance in radial direction; r_w , radial distance from center line to wall
 r' r/d
 N'_{Re} Modified Reynolds number dG_0/μ
 S Entropy, Btu/(lb mole)(°R)
 N'_{Sc} Turbulent Schmidt number $\mu/\rho E$
 T Temperature, °R
 t Temperature, °F; t_0 , of mixture before reaction
 T_r Temperature in the reactor
 T_0 Initial temperature prior to reaction
 V Volume of mixture
 \mathbf{V} Vector velocity, ft/hr
 V_c Volume of a batch reactor system per unit mass
 V_r Volume of a flow-type reactor
 y Mole fraction in the gas
 y_1^0 Mole fraction of the limiting component at the entrance to the reactor
 z Distance in axial direction
 z' z/d
 $*$ Designates activated complex
 λ Heat of reaction, Btu/lb of i
 μ Viscosity, lbs/(hr)(ft)
 ρ Density, lb/cu ft; ρ_i of component i in a mixture
 ρ_B Mass of catalyst per unit volume of bed, lb of catalyst/cu ft
 τ Time, hr

CHAPTER 12

SYNTHESIS OF AMMONIA

The synthesis of ammonia from nitrogen and hydrogen was the first chemical reaction to be carried out under high pressure on an industrial scale. This synthesis reaction has probably been studied more extensively and is better understood than other high-pressure reactions. It is free from side reactions and consecutive reactions, and from this standpoint its chemistry is simple. This process is well suited to serve as a typical example of the engineering of a high-pressure chemical process. The subject matter of the preceding chapters is needed to obtain an understanding of the process, and this example will serve to integrate the principles explained in the preceding chapters.

The names of Nernst,¹ Haber,² Carl Bosch, and A. Mittasch stand out from those of the early engineers and scientists responsible for the development of the first commercial synthesis. A pilot plant was operated at Ludwigshafen, Germany, in 1910 by the Badische Anilin & Soda Fabrik. A commercial plant began operation in 1913 with a capacity of 7,000 tons/year. World War I lent impetus to the increase in production capacity, and a number of modifications of the Haber process were developed over the subsequent years. These may be identified as the Haber-Bosch, the Claude, the Casale, the General Chemical Company, the Nitrogen Engineering Company, the Fauser, the Mont Ceniz, and the several plants erected during World War II and sponsored by the United States War Department and plants erected by corporations after the war. Of these the Claude differed to the greatest extent from the original Haber process. Over the years the best features of each have been adopted, and now all the processes bear a close resemblance to one another, differing chiefly in the range of operating pressure and the method of preparing the synthesis gas.

The capacity of the Leuna Works at Merseburg, Germany, in 1937 was over 600,000 tons/year, and the total synthetic capacity in Germany in 1937 was reported as 1,390,000 tons. A large amount of experimental work was done in the United States by the Fixed Nitrogen Research

¹ W. Nernst, *Z. Elektrochem.*, **13**:521 (1907).

² F. Haber, *Z. Elektrochem.*, **20**:597-604 (1914).

Laboratory in Washington, D.C., during the decade following World War I. This contributed to the development of catalysts for the reaction, determined the composition of the gases at chemical equilibrium, and provided designs for the special equipment required at high pressure. In the United States synthetic-ammonia production was started in 1921 by the Atmospheric Nitrogen Corporation at Syracuse, New York. Other plants were built later, and by 1932 there were 10 plants with a capacity of 316,500 tons/year. Of this capacity 275,000 tons were in two plants, the Atmospheric Nitrogen Corporation at Hopewell, Virginia, and E. I. du Pont de Nemours and Company at Belle, West Virginia. Ten additional plants with a capacity of 800,000 tons/year were constructed during World War II, and by 1956 the capacity in the United States had increased to 4,100,000 tons^{2a} of anhydrous ammonia per year.

Synthetic ammonia is the main source of nitrogen used to supply the needs of the chemical industry and of agriculture. During war time, the chief need has been for nitrogen for explosives. During peacetime, the chief need is for nitrogen for fertilizer, although numerous other uses consume large tonnages. The price is about \$90 per ton.

12-1. Chemical Equilibrium. The early determinations of the equilibrium state for the reaction of nitrogen and hydrogen were made by Haber and Van Oordt³ at about 1000°C and 1 atm, and only traces of ammonia were formed. Since the reaction is accompanied by a reduction of the reacting mixture from 2 volumes to 1 volume, it was apparent that an increase in pressure would cause the formation of a higher percentage of ammonia at equilibrium. Measurements by Haber and LeRossignol^{4,5} at 1 atm from 700 to 1000°C and later by Nernst¹ at 30 atm and by Jost⁶ at 72 atm demonstrated the quantitative effect of pressure on the reaction and provided reliable values of the equilibrium constant at several temperatures. The temperature range was extended from 700 down to 561°C at 30 atm by Haber.² A more thorough and extensive investigation of the equilibrium was carried out at the Fixed Nitrogen Research Laboratory by Larson and Dodge⁷ and by Larson.⁸ The range from 500°C down to 350°C was covered at pressures from 10 to 1,000 atm. The percentage of ammonia at equilibrium resulting from an initial 3:1 hydrogen-nitrogen mixture is shown in Table 12-1. These data are shown graphically in

^{2a} "Chemical Economics Handbook," pp. 703.33a and b, Stanford Research Institute, Stanford, Calif.; also *Chem. Eng. News*, **34**(3):203 (1956).

³ F. Haber and G. Van Oordt, *Z. anorg. Chem.*, **43**:111 (1904); *ibid.*, **44**:341 (1905).

⁴ F. Haber and R. LeRossignol, *Ber.*, **40**:2144 (1907).

⁵ F. Haber and R. LeRossignol, *Z. Elektrochem.*, **14**:181 (1908).

⁶ F. Jost, *Z. anorg. Chem.*, **57**:414 (1908).

⁷ A. T. Larson and R. L. Dodge, *J. ACS*, **45**:2918 (1923).

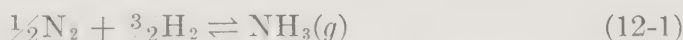
⁸ A. T. Larson, *J. ACS*, **46**:367-372 (1924).

TABLE 12-1. PERCENTAGE OF AMMONIA AT EQUILIBRIUM FROM A 3:1 MOLAL MIXTURE OF HYDROGEN AND NITROGEN†

Temperature, °C	Pressure, atm						
	10	30	50	100	300	600	1,000
200	50.66	67.56	74.38	81.54	89.94	95.37	98.29
250	28.34	47.22	56.33	67.24	81.38	90.66	96.17
300	14.73	30.25	39.41	52.04	70.96	84.21	92.55
350	7.41	17.78	25.23	37.35	59.12	75.62	87.46
400	3.85	10.15	15.27	25.12	47.00	65.20	79.82
450	2.11	5.86	9.15	16.43	35.82	53.71	69.69
500	1.21	3.49	5.56	10.61	26.44	42.15	57.47
550	0.76	2.18	3.45	6.82	19.13	31.63	41.16
600	0.49	1.39	2.26	4.52	13.77	23.10	31.43
650	0.33	0.96	1.53	3.11	9.92	16.02	20.70
700	0.23	0.68	1.05	2.18	7.28	12.60	12.87

† From A. T. Larson and R. L. Dodge, *J. ACS*, **45**:2918 (1923); and A. T. Larson, *ibid.*, **46**:367-372 (1924).

Figs. 12-1 and 12-2. For the reaction



Lewis and Randall⁹ calculated the value of ΔF° in calories per gram mole as a function of the temperature in degrees Kelvin. The value of $\log K$ from Harrison and Kobe¹⁰ is as follows:

$$\begin{aligned} \log K = & \frac{2250.322}{T} - 0.85340 - 1.51049 \log T \\ & - 25.8987 \times 10^{-5}T + 14.8961 \times 10^{-8}T^2 \end{aligned} \quad (12-2)$$

The value of the equilibrium constant is calculated from ΔF° by the equation

$$-\Delta F^\circ = RT \ln K \quad (12-3)$$

For this reaction

$$K = \frac{\bar{f}_{\text{NH}_3}}{\bar{f}_{\text{H}_2}^{3/2} \bar{f}_{\text{N}_2}^{1/2}} \quad (12-4)$$

K is constant at a given temperature and does not vary with pressure. That is, it changes with temperature only and not at all with pressure. The fugacities of each substance, nitrogen, hydrogen, and ammonia, vary

⁹ G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 357, McGraw-Hill Book Company, Inc., New York, 1923.

¹⁰ R. H. Harrison and K. A. Kobe, *Chem. Eng. Progr.*, **49**:349 (1953).

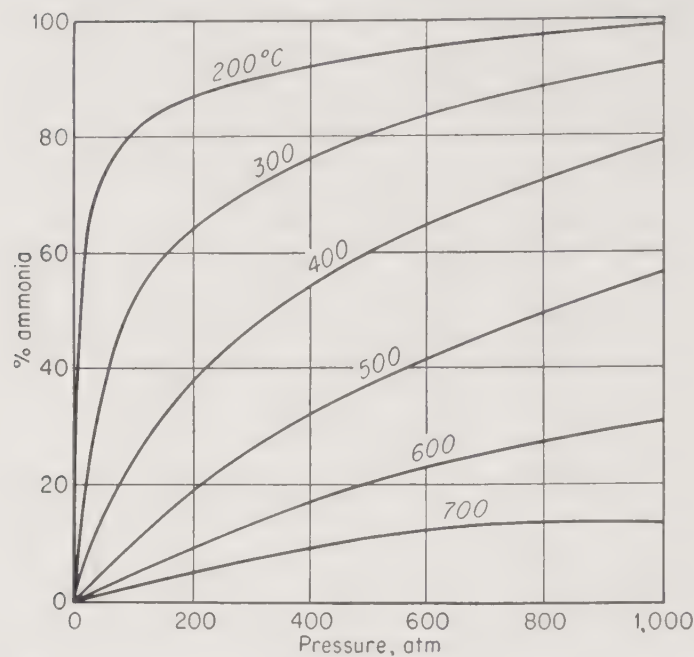


FIG. 12-1. Per cent ammonia at equilibrium from an initial mixture of 3:1 hydrogen-nitrogen gas.

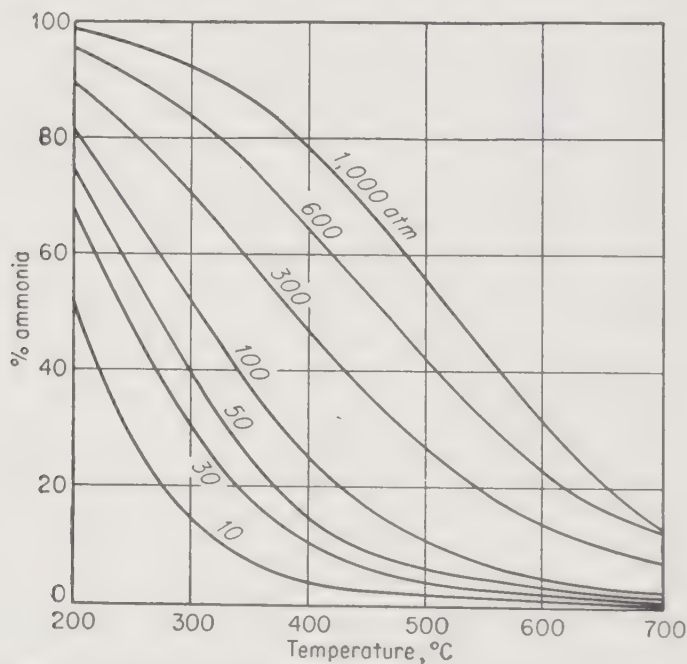


FIG. 12-2. Per cent ammonia at equilibrium from an initial mixture of 3:1 hydrogen-nitrogen gas.

with pressure, and consequently the proportion of each substance present in the equilibrium state will also vary with pressure. This accounts for the large change in per cent ammonia present at equilibrium when the pressure is varied at a constant temperature.

The equilibrium data make it clear that at any pressure higher percentages of ammonia will be possible at low temperatures than at high,

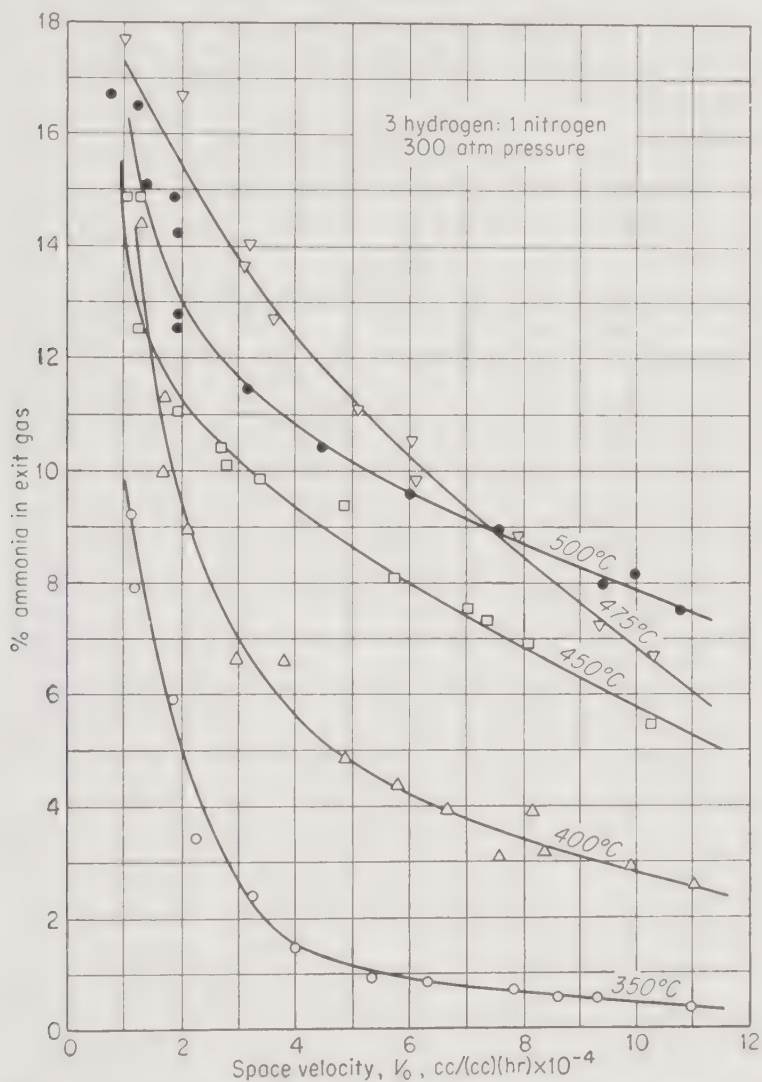


FIG. 12-3. Per cent ammonia in exit gas from an experimental reactor vs. the space velocity. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

and the lower the temperature at which the reaction will proceed, the more the equilibrium will favor the formation of ammonia. No catalyst has yet been found which will provide for the reaction to take place at the lower temperatures, and most commercial processes are carried out in the range between 425 and 600°C.

Similarly, at any temperature, an increase in the pressure will increase the possible per cent ammonia in the gases from the converter. The ammonia-synthesis processes operate at pressures from 200 to 1,000 atm. Within these ranges of temperature and pressure, reference to the equilibrium data will show that the per cent ammonia at equilibrium may vary from 9 to 75 per cent.

12-2. Rate of Ammonia Production. The reaction equilibrium at a given temperature and pressure sets upper limits to the amount of

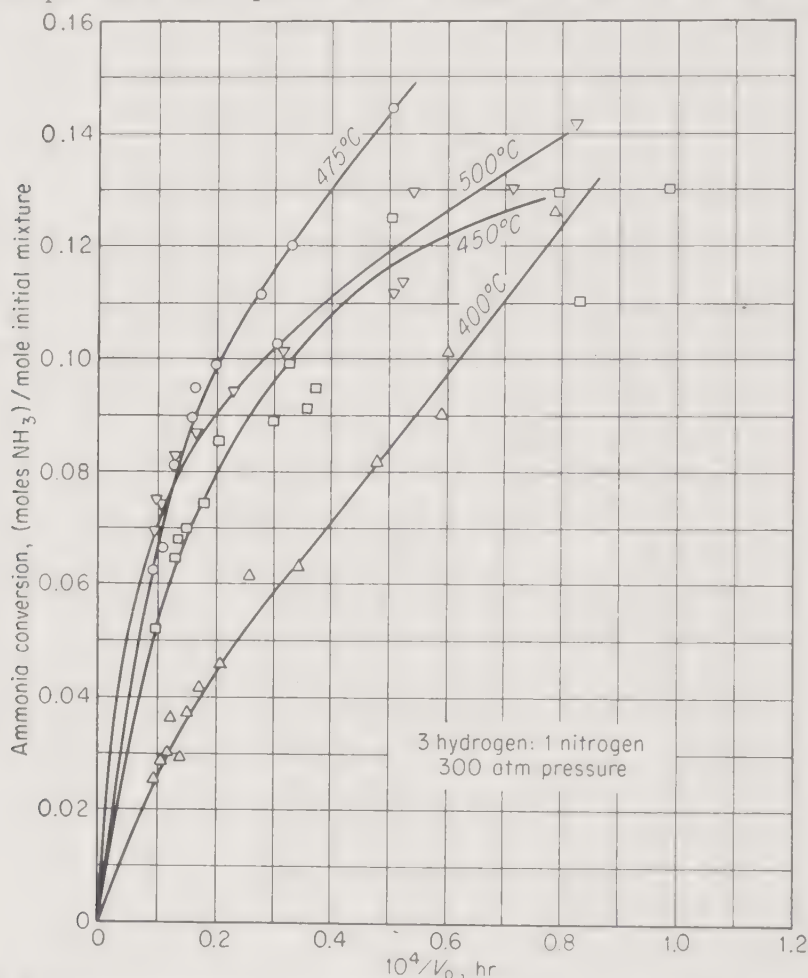


FIG. 12-4. Fractional conversion to ammonia vs. the reciprocal of the space velocity. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

ammonia it is possible to obtain from a given amount of hydrogen-nitrogen mixture as it passes once through the synthesis converter. The actual amount produced is always less than this. At high temperatures, the amount at the upper limit is small and the actual amount produced is near this limit. At low temperatures and moderate pressures, the amount at the upper limit is large, but the actual amount produced is small. This is because the rate of reaction is higher at the higher temperatures. A catalyst is necessary with this reaction in order that the

ammonia produced at moderate temperatures in the range from 400 to 600°C will approach the thermodynamically possible limit. The development and preparation of the catalyst will be described later.

The catalyst is composed of iron oxides promoted with potassium oxide and aluminum oxide. Figure 12-3 shows the variation of the per cent ammonia in the gas leaving an experimental reactor¹¹ as the space velocity is changed at a number of constant temperatures ranging from 350 to 500°C. In this case, the reactor is supplied with a gas mixture containing hydrogen and nitrogen in the mole ratio of 3:1 and at 300 atm pressure. The conversion to ammonia in moles of ammonia per mole of initial mixture is shown in Fig. 12-4 as it varies with the reciprocal of the space velocity. The reciprocal of the space velocity is related to the time that a given portion of gas is in contact with the catalyst. At a given temperature and pressure, a larger reciprocal space velocity corresponds to a longer time of contact with the catalyst. Longer time of contact results in greater conversion up to the thermodynamic limit.

In Fig. 12-5 the measurements shown in the two preceding figures have been used to determine the rate of ammonia formation per unit volume of catalyst. The rate of formation at any point in the catalyst is nearly independent of the space velocity and depends on the pressure, temperature, and per cent ammonia at that point. The rate of reaction decreases rapidly as the per cent ammonia in the gas increases. These experiments were carried out at a constant temperature. They indicate the behavior at any point where the temperature, pressure, and per cent ammonia are known in a reactor operating isothermally, adiabatically, or with a certain amount of heat being exchanged between the catalyst bed and the incoming gas stream.

¹¹ R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).

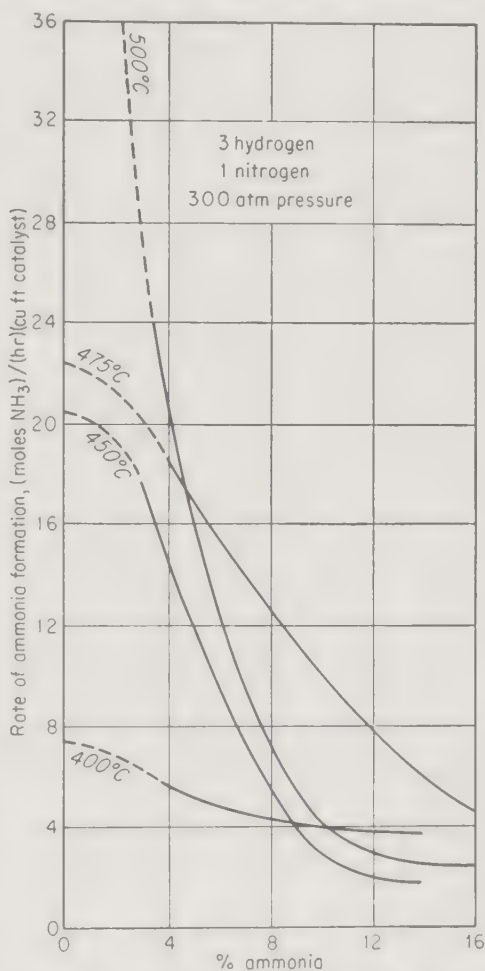


FIG. 12-5. Rate of ammonia formation per unit volume of catalyst. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

Since heat is given off during the reaction, this heat of reaction usually leads to a nonisothermal temperature distribution throughout the catalyst bed. The difference in heat capacity of reactants and products for the reaction of Eq. (12-1) is given by Glasstone¹⁰ as

$$\Delta C_p = -7.457 + 7.38 \times 10^{-3}T - 1.409 \times 10^{-6}T^2 \quad \text{cal/(g mole)}(^{\circ}\text{K}) \quad (12-5)$$

and the standard heat of reaction as

$$\Delta H^{\circ} = -9,130 - 7.46T + 3.69 \times 10^{-3}T^2 - 0.47 \times 10^{-6}T^3 \text{ cal/g mole}$$

and

$$\Delta H_{298}^{\circ} = -11,030 \text{ cal/g mole}$$

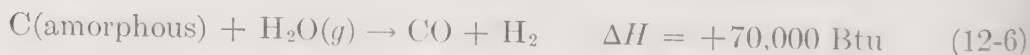
12-3. Preparation of Hydrogen-Nitrogen Mixture. The commercial synthesis of ammonia requires a plentiful, low-cost supply of both nitrogen and hydrogen. Nitrogen is obtained from the air, but it must be separated from oxygen, water vapor, and other contaminants sometimes in the air. Hydrogen is found combined with other elements in water, natural gas, and coal. It is freed from chemical combination and carefully purified to protect the catalyst from poisons such as water vapor, carbon oxides, oxygen, and hydrogen sulfide. The separation and purification of hydrogen and nitrogen are usually carried out simultaneously. In addition to air and water, the older ammonia-synthesis plants used coal, while the majority of the plants constructed since World War II have used natural gas. The production of hydrogen and nitrogen will be discussed first as separate processes.

Hydrogen. The commercial production of hydrogen is chiefly dependent on four sources

1. Water gas
2. Natural gas
3. Coke-oven gas
4. Electrolysis of water

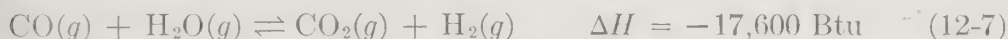
Hydrogen has been obtained also from the reaction between steam and iron and as by-product hydrogen from electrolytic chlorine cells. Other reactions have been proposed.

The manufacture of *blue water gas* is based on the reaction



The reaction is carried out by passing steam over incandescent coke or coal at a temperature of 1000°C or higher. The large heat absorption by the endothermic reaction cools the coke, and the process is, therefore, carried out in cycles consisting of an air blow followed by a steam blow.

Part of the coke is burned during the air blow and heats the bed to incandescence. The steam blow then generates the blue water gas and cools the bed. The composition of the gas is generally about 50 per cent H_2 , 40 per cent CO , 4 to 6 per cent CO_2 , and 4 to 6 per cent N_2 . The nitrogen enters from incomplete purging after the air blow. The carbon dioxide is formed by the reactions.



The first of these reactions is the basis of the *catalytic water-gas* reaction, also called the water-gas conversion or shift reaction. The conversion at equilibrium for this reaction is not favorable to converting carbon monoxide and steam to carbon dioxide and hydrogen at the temperatures encountered in the blue-water-gas converter. In fact, at temperatures above $1000^\circ C$ carbon monoxide is more stable than carbon dioxide in the presence of either carbon or water vapor. At lower temperatures the equilibrium shifts, and at temperatures approaching $500^\circ C$ and lower, and in the presence of a catalyst, the conversion of carbon monoxide and water vapor to hydrogen and carbon dioxide takes place readily. Thus in the commercial production of hydrogen, blue water gas is passed through a shift converter to convert carbon monoxide to hydrogen. The gas-phase reaction is slow at these low temperatures, and a catalyst is necessary to make it commercially feasible. The equilibrium for this reaction is shown in Table 12-2. The percentage of carbon monoxide left in the converted gases and the ratio of steam to water gas to be employed are determined by an economic analysis which considers the cost of the excess steam used, the value of the hydrogen produced, and the cost of removing the unconverted carbon monoxide by other means. The ratio of steam to water gas is commonly in the vicinity of 3:1 in commercial plants.

The percentages given in Table 12-2 are the minimum values determined by thermodynamic calculations. The catalyst developed for the reaction permits commercial operation at a temperature of $500^\circ C$ and lower. The composition of a representative gas after catalytic conversion is 65 per cent H_2 , 30 per cent CO_2 , 2 per cent CO , and 3 per cent N_2 and inert gases. The catalysts for commercial operation are oxides of iron with promoters such as chromium or cerium oxides. Evans and Newton¹² found that mixtures of cobalt-aluminum-potassium oxides were best for low-temperature operation at 380 and $444^\circ C$. The cobalt oxide mixture is best at the lower temperatures, but this is subject to sulfur poisoning to a greater extent than the iron oxide mixture. A fused cobalt oxide catalyst promoted with a large amount of copper was developed at the

¹² R. M. Evans and W. L. Newton, *Ind. Eng. Chem.*, **18**:513 (1926).

Fixed Nitrogen Research Laboratory. This was effective for the water-gas conversion at 300°C and at a space velocity of 5,000 without appreciable formation of methane.

TABLE 12-2. PERCENTAGE OF CARBON MONOXIDE (DRY, CARBON DIOXIDE-FREE BASIS) AT EQUILIBRIUM FROM A GAS MIXTURE CONTAINING INITIALLY 33% CO, 42% H₂, AND 25% N₂†

(Calculated from water-gas equilibrium constants given in column 2)

Equilibrium temperature, °C	Equilibrium constant K_p	Ratio steam to water gas, %			
		2:1	3:1	4:1	5:1
283	0.0143	0.21	0.128	0.10	0.072
310	0.0217	0.32	0.20	0.15	0.114
380	0.054	0.77	0.49	0.35	0.29
444	0.105	1.44	0.92	0.68	0.55

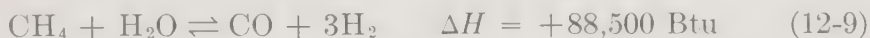
† From G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 357, McGraw-Hill Book Company, Inc., New York, 1923; and P. H. Emmett, "Fixed Nitrogen," H. A. Curtis, editor, Chemical Catalog Company, Inc., New York, 1932.

A subsequent step in the commercial preparation of the hydrogen is the removal of the carbon dioxide by scrubbing with water under about 25 atm pressure in a countercurrent absorption system. The carbon dioxide concentration is reduced by this means to approximately 1 per cent in the scrubbed gases. The power requirement for pumping the water against a pressure of 25 atm is reduced about 50 per cent by discharging the water from the scrubber against a Pelton water wheel which recovers part of the energy for reuse in the pumps. In an alternative method, the pressure causes the water to flow up a hill as at the plant at Belle, West Virginia. The absorbed carbon dioxide is released at atmospheric pressure, and the water then flows downhill, regaining its pressure. The pumps must supply energy to overcome the fluid friction in the pipes leading up and down the hill.

The removal of the last 1 per cent of carbon dioxide and any hydrogen sulfide remaining in the gas may be carried out at a pressure of 200 atm in a scrubber using monoethanolamine. This is followed by a cuprous formate scrubber to remove the carbon monoxide. The last traces of carbon oxides and water vapor must be removed. This is accomplished by various methods, such as by using 25 per cent caustic solution at 260°C and a low-temperature trap to freeze out the water and collect ammonium carbamate. Soda lime or sodamide has also been used to eliminate the last few hundredths of a per cent of water vapor. The last traces of

carbon monoxide may be converted to methane in a catalytic reactor called a methanator.

Ammonia-synthesis plants built during and after World War II have used *natural* or *refinery gas* as a source of hydrogen.²² Methane or other paraffinic or olefinic hydrocarbon gases are used. These are first preheated and passed through trays of bauxite which serve as a catalyst and remove the sulfur. They then react with steam in a reformer furnace at gas temperatures up to 1300°F over an alumina-base catalyst. This is a continuous process with the catalyst contained in high-chromium-alloy steel tubes heated from the outside to 1700°F. A typical reaction is¹³



Preheated steam, air, and additional methane are introduced in the next step to supply nitrogen in the proper percentage for ammonia production. The unconverted methane from the reformer furnace, as well as that added, together with part of the carbon monoxide, are selectively oxidized in a combustion chamber. The gases leaving this combustion chamber have a temperature of 2000°F and are composed of 40 per cent H₂, 11 per cent CO, 4 per cent CO₂, 28 per cent H₂O and 17 per cent N₂. This gas is quenched to 800°F and passed through a converter charged with iron-base catalyst to carry out the water-gas conversion reaction replacing the carbon monoxide content with hydrogen and carbon dioxide. The carbon dioxide is scrubbed out of the gases using monoethanolamine as an absorbent at 200/psi. The carbon dioxide is driven off from the monoethanolamine by heating it with steam, and the regenerated monoethanolamine is then recycled to the absorbing system. The last traces of carbon monoxide are removed at 140 atm by absorption in a mixture of cuprous and cupric formate.

The gas from *by-product coke ovens* for the production of metallurgical coke contains a high percentage of hydrogen. A typical gas composition is 49.2 per cent H₂, 30.3 per cent CH₄, 9.2 per cent N₂, 5.5 per cent CO, 2.3 per cent C₂H₄ and other illuminants, 1.8 per cent CO₂, 0.9 per cent C₆H₆, and 0.8 per cent O₂. The hydrogen may be separated from this type of gas as well as from water gas by liquefaction at low temperature and fractional distillation of the several components. This source of hydrogen has been employed in Europe, but the method has not been considered economically feasible in the United States.

In locations where electric power is cheap, 99.5 to 99.9 per cent pure hydrogen is manufactured by the electrolysis of water into hydrogen and oxygen. The design and operation of cells of this type are described more

¹³ R. N. Shreve, "The Chemical Process Industries," p. 130, McGraw-Hill Book Company, Inc., New York, 1945.

completely elsewhere.¹⁴ The process will be outlined briefly here. A direct current is passed through a 10 to 25 per cent aqueous alkali solution in a cell of one of several designs. As an illustration, one cell uses an iron cathode and a nickel-plated iron anode separated by an asbestos diaphragm to keep the oxygen and hydrogen apart. A temperature between 60 and 70°C is maintained, and the normal voltage per cell is greater than 2.0 and as high as 2.5 volts. The cells produce about 7.0 cu ft of hydrogen per kilowatthour. An interesting modification is the pressure electrolytic cell developed in Germany by Noeggerath.¹⁵ It is claimed that in tests hydrogen has been produced directly under 300 atm pressure and that higher pressures are possible. The problems of construction of such a cell are said to have been solved. Separate cylinders are used for the generation of the hydrogen and oxygen to prevent mixing. The level of electrolyte in the anode and cathode cylinders is maintained at the proper height by an automatic pressure equalizer. The oxygen is 99.1 per cent pure, and the hydrogen 99.9 per cent. The chief advantage seems to be in the elimination of the compressors required to increase the pressure of the hydrogen from atmospheric-pressure cells. The inventor also claims a higher electric efficiency for the pressure cells.

Nitrogen. The methods used to separate the nitrogen in the air from the oxygen and other gases differ from one process to another. The oxygen in the air may be allowed to react with coke, methane, hydrogen, or even ammonia; and the carbon oxides, water, and nitric acid formed are removed, leaving relatively pure nitrogen. Reactions for removing the oxygen may also be used for preparing the hydrogen.

Coke reacts with the oxygen of the air in a standard gas producer, and the *producer gas* formed has the following range of composition.¹⁶

	%		%
N ₂	50-56	CO ₂	9-3
CO	20-30	CH ₄	3-0.5
H ₂	20-8	O ₂	0.1-0.3

The high nitrogen content of this gas makes it an excellent source of this element. The hydrogen is derived partly from coal used in the producer and partly from steam added with the air to absorb excess heat. High hydrogen and carbon dioxide contents result from the use of excess steam. The carbon monoxide may be converted to hydrogen and carbon dioxide in the shift reaction, and this hydrogen together with that in the pro-

¹⁴ C. L. Mantell, "Industrial Electrochemistry," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

¹⁵ J. E. Noeggerath, *Chem. & Met. Eng.*, **35**:421 (1928).

¹⁶ J. Griswold, "Fuels, Combustion, and Furnaces," p. 225, McGraw-Hill Book Company, Inc., New York, 1946.

ducer gas is used in the synthesis mixture. Gas of nearly the same composition as producer gas (made without steam) is generated in the air blow of a water-gas set. The blow gas and run gas from a water-gas set may thus be combined to yield the proper 3:1 hydrogen-nitrogen ratio after conversion of the carbon monoxide and removal of the carbon dioxide.

In the plants in the United States using natural gas, the oxygen of the air is used to burn the hydrocarbons plus some of the carbon monoxide in the gas from the reformer furnace. In both these cases, the oxygen removed from the air is combined with the carbon from the hydrocarbons in preparing the hydrogen for the synthesis mixture. The ammonia from the synthesis reaction is sometimes burned with air over a catalyst and converted to nitric acid. This process serves to remove the oxygen from the air, and the remaining nitrogen can be used for the synthesis mixture. Because of the high ratio of air to ammonia used in the burners, only a small per cent of the ammonia production need be converted to nitric acid to supply the nitrogen requirements for the total production. This method is used in the Italian process patented by Fauser. The gases from the absorption towers in the ammonia-oxidation unit are purified and used to supply the nitrogen for the synthesis.

The gases in the air are also separated by fractional distillation at low temperatures where the differences in their boiling points may be used for distillation and absorption operations. The liquefaction of air by the Linde, Claude, and other processes provides a source of liquid air which may then be fractionated. Pure-oxygen manufacture in tonnage quantities has been developed,¹⁷ and this is providing a source of pure nitrogen from the low-temperature fractional distillation.

Partial Oxidation of Hydrocarbons. Air or tonnage oxygen is used to partially oxidize methane in natural gas¹⁸ to yield hydrogen. The partial oxidation of methane^{19,20,21} may be represented by the chemical equation



This undoubtedly takes place in two steps. First, the oxygen reacts with part of the methane to form carbon dioxide and water.



¹⁷ W. E. Lobo, *Chem. Eng. Progr.*, **1**:21 (1947).

¹⁸ J. C. Kelley and J. H. Cain, ACS National Meeting, Petroleum Chemistry Division, *Preprint* 28, September, 1953.

¹⁹ B. J. Mayland and G. E. Hayes, *Chem. Eng. Progr.*, **45**:452 (1949).

²⁰ C. W. Montgomery, E. B. Weinberger, and D. S. Hoffman, *Ind. Eng. Chem.*, **40**:601 (1948).

²¹ R. Mungen and M. B. Kratzer, *Ind. Eng. Chem.*, **43**:2782 (1951).

This reaction is strongly exothermic. The carbon dioxide and water then react with the remaining methane to produce carbon monoxide and hydrogen.



These reactions are endothermic, and the net result is slightly exothermic. Reaction (12-11) is rapid, while reactions (12-12) and (12-13) are slower and are the rate-determining reactions. In the absence of a catalyst, a temperature in excess of 2000°F is required to attain satisfactory reaction rates. The preheat temperature of the methane is limited to less than 1200°F by thermal cracking, and the preheat temperature of the oxygen is kept to the same level by the resistance of the tubes to oxidation. The required temperature is reached by using excess oxygen. The heat from reaction (12-11) raises the temperature and accounts for the presence of carbon dioxide and water vapor in the exit gas. The formation of carbon is practically eliminated by proper furnace design and by controlling the ratio of oxygen to methane.

A plant¹⁸ using tonnage oxygen is the first to attempt to purify completely the synthesis gas. Low-nitrogen natural gas is then a distinct advantage, since it reduces the cost of the partial-oxidation equipment. The partial-oxidation and purification steps are carried out under 300 to 400 psi pressure. The gases occupy a smaller volume at elevated pressure, and this entails a lower equipment cost. Lesser costs are also involved because the reactants, rather than the product hydrogen, are compressed since the reaction is accompanied by an increase in volume. A packaged oxygen unit supplies 95 per cent oxygen for the partial-oxidation unit and pure nitrogen for mixing with the hydrogen. After partial oxidation, the carbon monoxide in the gas is converted to carbon dioxide and hydrogen in a shift catalytic converter. The carbon dioxide is removed by scrubbing with an aqueous ethanalamine solution. The process gas now contains nearly pure hydrogen, and this is chilled and dried with activated alumina. This is necessary to prevent icing in the next operation.

Small concentrations of methane, carbon monoxide, and argon still remaining in the hydrogen gas are removed by scrubbing with liquid nitrogen. This removes inert gases so that the need for purging of the synthesis loop is substantially reduced. The needless compression of the inert gases is eliminated, and approximately the same conversion can be obtained at 3,600 psi as formerly obtained at 5,000 psi. Complete purification permits a considerable saving in compression cost. The synthesis gas from the liquid-nitrogen scrubber contains considerable nitrogen, and

the final mole ratio is adjusted by the addition of pure gaseous nitrogen from the oxygen unit.

12-4. A Low-pressure Process. There is no single standard ammonia-synthesis process. Improvements and modifications continue to be made. The economic factors at each plant location dictate variations in the source of hydrogen and nitrogen, in the method of preparation and purification of the synthesis-gas mixture, in the operating conditions in the reactor, in the design and arrangement of the reactors, and in the method of recovering the ammonia. Two complete processes will be described as typical examples, and variations in these will be considered.

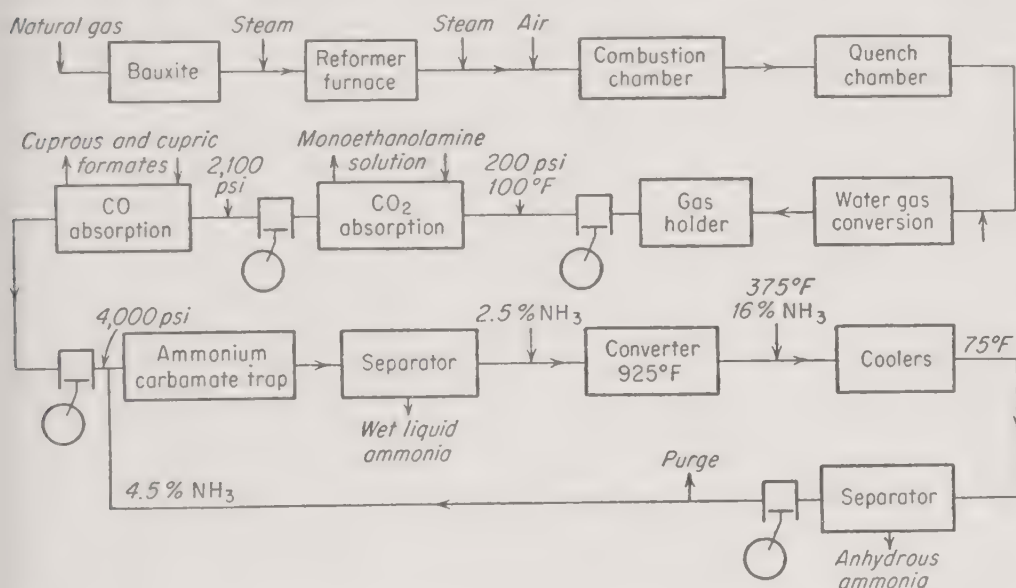


FIG. 12-6. Ammonia process using reformed natural gas at 300 atm. [From J. A. Lee, *Chem. Eng.*, 52(12):94, 134 (1945).]

The various processes now in use carry out the synthesis either at a relatively low pressure in the vicinity of 350 atm or at a higher pressure near 1,000 atm.

The first large-scale commercial plants operated in the low-pressure range. These were the German plants at Oppau and Merseburg. Modifications of these early designs account for the major part of the synthetic-ammonia capacity in the world today. In the early plants in Germany and also in the early plants built in the United States, the 3:1 hydrogen-nitrogen mixture was obtained by mixing water gas and producer gas in the proper proportions. Most of the more recent plants in the United States obtain their hydrogen from the reaction of natural gas with steam. A flow sheet for a process of this latter type²² is shown in Fig. 12-6. The natural gas is heated and passed over a bauxite catalyst

²² J. A. Lee, *Chem. Eng.*, 52(12):94, 134 (1945).

to remove sulfur. It is mixed with steam and allowed to react to produce carbon monoxide and hydrogen in a tubular reformer furnace containing a nickel catalyst at a temperature of up to 1300°F. The reforming reaction is endothermic, and heat is supplied through the reactor-tube walls. Preheated air and steam, and additional natural gas, are then added to the gases leaving the reformer furnace. These enter a combustion chamber where the unconverted methane and other hydrocarbons as well as some carbon monoxide react with the oxygen of the air. The temperature is then lowered and the water vapor content raised by contact with water in a quench chamber. The resulting gases are passed to a catalytic water-gas conversion reactor. The carbon dioxide in the gas leaving this reactor now amounts to about 16 per cent with less than 1 per cent carbon monoxide. The carbon dioxide is removed in an absorption tower at 200 psi pressure using monoethanolamine solution, as a solvent, flowing countercurrent to the gases in a Gerbitol system. The carbon dioxide is driven out of the spent monoethanolamine solution by heating it with steam, and the regenerated solution is recycled to the absorption tower.

The pressure of the remaining gas is now raised to 2,100 psi, and the last traces of carbon monoxide are removed in an absorption tower operated at this pressure with the gas flowing countercurrent to a solution of cuprous and cupric formate. This solution forms a chemical compound with the carbon monoxide which is easily broken down by heating with steam to regenerate the solution. The gas may contain traces of acetylene, which forms cuprous acetylide (highly explosive when dry) by combining with cuprous formate. The acetylide is removed in the harmless wet state. The gas now passes to the reactor loop. Unreacted gas from the synthesis reactor is recycled and mixed with purified incoming gas mixture. The last traces of carbon dioxide react with a small percentage of ammonia introduced with the recycle gas and form ammonium carbamate by the reaction



This is removed in ammonium carbamate traps at about 100°F, the gas is then chilled to 25°C, and liquid ammonia is condensed out. The introduction of the make-up gas upstream from the final ammonia condenser is practiced to take advantage of the gas-cleansing action of this condenser. Impurities such as oil aerosol particles from the compressors, carbon dioxide, and moisture are removed in this manner.

Gas containing about 2½ per cent ammonia is sent to the converter. The cool gas is heated by the gases leaving the converter and by heat exchangers within the converter. The temperature of the product gases is lowered to 375°F before they leave the converter. The reaction in the converter catalyst bed takes place at about 4,000 psi and 925°F. The

converters are tall, cylindrical vessels and will be described later. The product gases containing 16 per cent ammonia pass through additional heat exchangers and coolers to condense part of the ammonia content at 75°F as anhydrous ammonia. Liquid ammonia is removed in a separator, and 4.5 per cent ammonia remains in the gases leaving the separator. Part of this gas is bled off or purged to remove the inert gases methane and argon and small excesses of either nitrogen or hydrogen which would otherwise accumulate in the recycled gas. The remaining gas is passed through a booster compressor to return it to the converter inlet and is then mixed with the incoming make-up gas. A number of the steps in the process will be discussed in more detail later.

12-5. A High-pressure Process. The Claude process was the original high-pressure process. In recent years the ammonia plants at Morgantown, West Virginia, Louisiana, Missouri, and at Yazoo City, Mississippi, have been built as modifications of the early designs. The flow sheet for the plant at Yazoo City is shown in Fig. 12-7. Some of the steps in the process are similar to those in the low-pressure process. The plant,²³ with a capacity of 120 tons of anhydrous ammonia per day, was designed to reduce investment costs to the extent that could be justified economically, and the process is somewhat less complex than earlier designs.

Preparation of Synthesis Gas. A natural-gas and flue-gas mixture is treated with activated carbon to remove sulfur and is then mixed with steam and recycled nitrogen and passed through a tubular reformer furnace. This furnace operates at a sufficiently high temperature to obtain complete reforming of the methane in one step to yield carbon monoxide and hydrogen. The tubes are filled with nickel-base catalyst on a diatomaceous-earth carrier. Recovery of latent heat as well as sensible heat from the hot reformed gas is not feasible in a waste-heat boiler, but this can partly be accomplished in a heat exchanger and water heater-saturator arrangement. One 12-ft-diameter carbon-steel vessel 65 ft high is used. It consists of two separate sections, one above the other. The upper section is packed with 15 ft of 3-in. Raschig rings, and the lower with 25 ft. The lower section serves as the saturator for the gas going to the shift converter, and the upper section recovers heat from the gas leaving the shift converter and heats the water used in the saturator. Gas from the shift converter enters the bottom of the upper section, flows countercurrently to quenching water, heats the quenching water to nearly boiling, and passes out the top of the tower to the gas cooler. The hot water passes down into the lower section, where it meets gas from the reformer coming from the tube side of the heat exchangers. This gas becomes saturated with steam in the lower section of the tower, passes out the top of the bottom section, through the shell side of the heat

²³ Will H. Shearon, Jr., and H. L. Thompson, *Ind. Eng. Chem.*, **45**:1242 (1953).

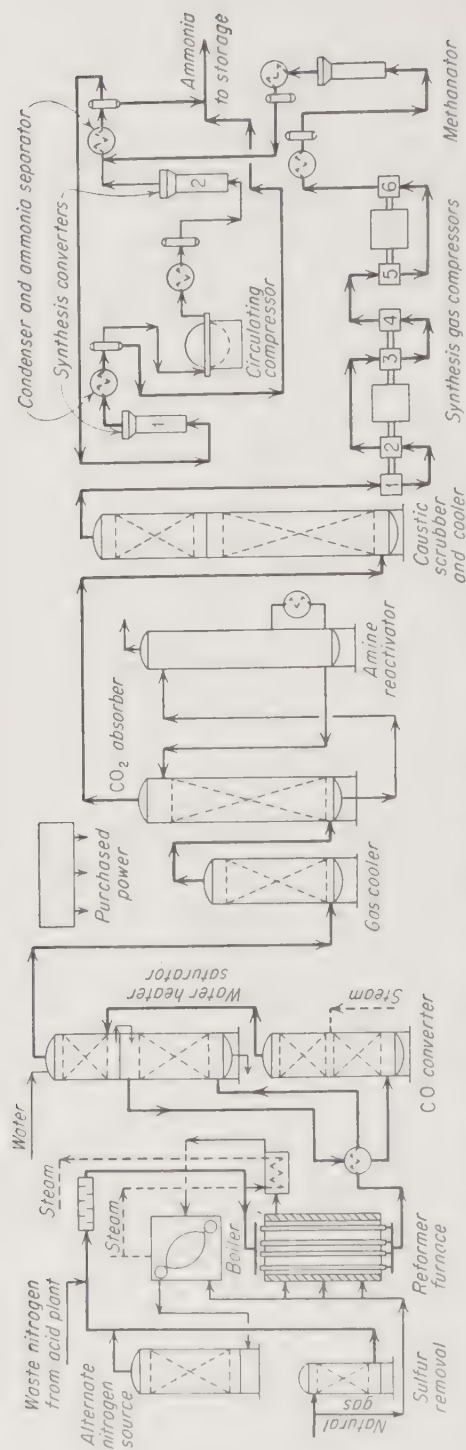


FIG. 12-7. Ammonia process using reformed natural gas at 1,000 atm. [From W. H. Shearon, *Ind. Eng. Chem.*, **44**:254 (1953).]

exchangers, and on to the shift converters. Here the carbon monoxide reacts with steam, in the presence of an iron-chromium catalyst, and forms carbon dioxide and additional hydrogen. The hydrogen and nitrogen which later react to form ammonia are now present in the gas, and their concentrations are in the proper ratio for the synthesis reaction. The gas also contains a large percentage of carbon dioxide.

The gas from the shift converter is cooled, and the carbon dioxide is absorbed by amine solutions followed by a caustic scrubber. This method provides for the preparation and purification of the synthesis gas at near atmospheric pressure. Compared to purification at high pressure, this method avoids the handling of large volumes of liquid under pressure, complicated compressor design and operation, and increased compressor investment costs. The compression is carried out at one point after all purification except final carbon monoxide removal has been completed. The last traces of carbon monoxide are removed by methanation. This step is carried out at 15,000 psi and in the temperature range of 730 to 930°F in this plant. Methanation is the reverse of the reforming reaction, converting carbon monoxide to methane over an iron catalyst similar to the ammonia-synthesis catalyst. It replaces the more conventional, but also more complicated and expensive, copper-liquor system which, however, involves no consumption of hydrogen as in methanation. The methanation reactor uses approximately half as much catalyst as the ammonia-synthesis reactor, and the catalyst life is twice as long. The carbon monoxide in the synthesis gas is reduced to as low as 0.0001 per cent by methanation at synthesis pressure, as opposed to 0.01 per cent when carried out at atmospheric pressure.

The Synthesis Loop. The ammonia-synthesis reactors operate at 15,000 psi and in the temperature range from 900° to 1150°F, depending on the catalyst activity. The per cent ammonia at equilibrium is shown in Figs. 12-1 and 12-2. Because of the imperfect approach to equilibrium and the incomplete conversion at equilibrium, ammonia must be removed from the partially reacted gas mixture and the unreacted gas must be returned to a reaction zone. Conventional low-pressure plants use one converter and recycle the gas as shown in Fig. 12-6. In the plant at Yazoo City, two converters are used in series and the gas is recirculated. Arranging the converters in series rather than in parallel requires a lower-capacity recirculating pump, permits the conversion load to be varied between the converters by employing bypass valves, and allows the flow through the converters to be reversed to lengthen the over-all catalyst life.

The construction and operation of the synthesis converter are covered in a following section. Synthesis gas enters the circulatory system after the second converter and mixes with the recycle stream containing

ammonia and a predetermined accumulation of inerts. The ammonia is condensed and separated, and the stream passes to the first converter, which normally carries about 60 per cent of the conversion load. The ammonia is condensed from the gas leaving this converter. The gas then passes through the circulator, which restores the 500 to 1,000 psi pressure drop, is cooled, passes through a water and oil separator, through the second converter, and through the precooler to the ammonia condenser at the beginning of the cycle. In one pass through the two converters, approximately 45 per cent of the hydrogen and nitrogen in the gas is converted to ammonia, about 80 per cent of the ammonia in the gas is recovered in the separator following the first converter, and 68 to 72 per cent in that following the second, leaving a residual concentration of ammonia in the recycled gas stream of 4 to 6 per cent. Earlier Claude plants used expensive alloys extensively in their construction. Current experience indicates that carbon steel is quite satisfactory for equipment and piping.

A small amount of methane was formed in the methanator, and this and other inert gases tend to accumulate in the circulatory system. The increased concentration of inert gases causes a reduction in the per cent ammonia at equilibrium and requires continuous purging to maintain the inerts at an acceptable concentration. The main purge is taken from the circulatory line following the second converter and immediately preceding the point of introduction of fresh synthesis gas. The ratio of nitrogen and hydrogen to inerts is at a minimum at this point. Some gas dissolves in the liquid-ammonia condensate, and this gas, which serves as a purge, is removed from the two separators. Ammonia is recovered from the purge gas which normally analyzes 20 per cent methane, 19 per cent nitrogen, 58 per cent hydrogen, and 3 per cent argon, and contains about 10 per cent of the original nitrogen and hydrogen in the incoming synthesis gas.

At 1,000 atm, the conversion per pass through the synthesis reactors is considerably greater than at lower pressures. Only about one-seventh as much catalyst and converter volume is necessary to produce the same quantity of ammonia; and about one-fifth as much gas must be pumped and piped on the basis of actual volume at synthesis conditions. The catalyst life is only about 3 months in this process, and this shorter life requires that the design of the converters permit a rapid change in catalyst in order to avoid a serious production loss. This change is accomplished in one 8-hr shift.

12-6. The Catalyst. During the development of the synthetic-ammonia process little was known of the mechanism of the catalyst action. The commercial catalysts were, therefore, developed largely by a cut-and-try method. Paralleling this development, research has been carried on with a more fundamental approach to the question of catalyst mechanism.

This research can no doubt be looked upon as the principal source of catalyst improvements in the future. The recent concepts of the catalyst mechanism are dealt with briefly in Chap. 11. The development of the ammonia catalyst will now be discussed.

Development. Active interest in the direct synthesis of ammonia resulted from the discovery that iron is an effective catalyst for the reaction. Other catalysts for this reaction were sought as well as other combinations with iron. Many materials were found to have catalytic action to varying degrees. Test results have been published on iron, cobalt, nickel, tungsten, and molybdenum.²⁴ Of these materials, only iron has been extensively developed as the principal catalytic constituent. The catalyst was at first prepared by mixing precipitated oxides of iron and other metals, or their nitrates, and igniting these to form the anhydrous oxides. The oxides were then reduced to the metallic state, with 3:1 hydrogen-nitrogen gas in the catalyst chamber of the reactor. The catalyst was then in a porous, active form, and, to preserve its activity, it was kept continuously in contact with the carefully purified and dried reducing atmosphere of the hydrogen-nitrogen synthesis-gas mixture.

Later a fusion method²⁵ was adopted. This consisted of first burning the iron to an oxide which was fused, and other materials were added to the molten oxide. The melt was then cooled and crushed to the preferred particle size. This method produces a more rugged catalyst which withstands handling without crumbling or powdering.

At 30 and 100 atm, the activity of pure-iron catalysts was observed to be greatest when a mixture of oxides was used. The best mixture consisted of a ratio of 1:1 ferrous to ferric iron. A pure-iron catalyst is relatively effective at temperatures below 450°C and at pressures of 200 atm or less. The original catalysts for the Haber process lost their activity at higher pressures, and it was thought that the process might be limited to pressures below 250 atm. In order to provide a more active catalyst and to avoid these limitations, other constituents were mixed with the iron. First, other catalytically active materials were used. These mixtures were usually less active than the iron alone at low temperatures. At temperatures above 500°C, a 1:1 mixture of iron and molybdenum retained its activity, while the activity of pure iron decreased rapidly. This loss of activity at high temperatures is commonly attributed to *sintering*. This is not necessarily so pronounced a sintering as is associated with metallurgical processes, but at temperatures well below the softening point there appears to be enough movement or rearrangement of the molecules in the catalyst surface to reduce greatly their catalytic activity.

A second step in the addition of other materials to the iron catalyst

²⁴ A. T. Larson and A. P. Brooks, *Ind. Eng. Chem.*, **18**:1305 (1926).

²⁵ A. T. Larson and C. N. Richardson, *Ind. Eng. Chem.*, **17**:971 (1925).

was the addition of substances which show little or no catalytic activity by themselves. The oxides more difficult to reduce, such as the oxides of aluminum and silicon, have high melting points and would be expected to reduce the sintering action at high temperatures. Certain of these materials resulted in a pronounced increase in catalyst activity.^{2,25a} An iron catalyst operated at 450°C, a space velocity of 5,000, and 100 atm pressure produced only 3 to 5 per cent ammonia in a pure 3:1 hydrogen-nitrogen gas, whereas iron containing a few per cent aluminum oxide produced 8 to 9 per cent ammonia. The increase in catalyst activity with the addition of small percentages of catalytically inert compounds is termed *promoter action*.

The addition of two such compounds^{26,27} resulted in a doubly promoted catalyst. The *doubly promoted catalysts* displayed a greater activity than the singly promoted. The two promoters consisted of an acidic or amphoteric oxide, such as aluminum oxide, zirconium dioxide, silicon dioxide, or titanium dioxide, together with an alkaline oxide, such as potassium oxide or sodium oxide. The pronounced action of these promoters is illustrated by the per cent ammonia found in the effluent gas when a pure 3:1 hydrogen-nitrogen mixture is passed over the three types of catalyst at 100 atm pressure, a space velocity of 5,000, and 450°C. The pure-iron catalyst produced 3 to 5 per cent ammonia, the singly promoted catalyst 8 to 9 per cent, and the doubly promoted 13 to 14 per cent. The percentage of ammonia at equilibrium in this case is 16.43. The addition of two oxides of the same class is not so effective as the addition of oxides from both classes. In fact, the promoter action of potassium oxide is apparently dependent upon the presence of a hard-to-reduce oxide as another component in the catalyst. When such an oxide is not also present, the potassium oxide may have a deleterious effect. The influence of single and double promoters is shown clearly in Table 12-3.

The doubly promoted catalyst remains active at higher pressures, even up to 1,500 atm, and permits operation over a wider range of pressures and temperatures. Because of its increased activity, it is possible to operate economically at lower temperatures, especially in the range of 450 to 475°C and below. The thermal resistance of the catalyst and the lower-temperature operation both result in longer catalyst life. The high per cent ammonia in the reacted gases, approaching the equilibrium value, increases the plant capacity and simplifies the problem of condensing the ammonia. These active catalysts are usually more sensitive to catalyst poisons, and a more careful purification of the reaction gas is necessary

^{25a} P. H. Emmett, in H. A. Curtis, editor, "Fixed Nitrogen," Chemical Catalog Company, Inc., New York, 1932.

²⁶ A. T. Larson, U.S. patent 1,489,497.

²⁷ A. T. Larson, *Ind. Eng. Chem.*, **16**:1002 (1924).

TABLE 12-3. PERCENTAGE OF AMMONIA IN REACTION GASES FROM SINGLY AND DOUBLY PROMOTED IRON CATALYSTS AT 450°C AND 5,000 SPACE VELOCITY†

Promoters	Ammonia, %	
	30 atm	100 atm
1.01% Al_2O_3	5.02	9.0
0.35% K_2O + 0.84% Al_2O_3	5.82	13.60
0.61% ZrO_2	4.88	7.72
0.96% K_2O + 2.76% ZrO_2	5.43	12.73
0.51% SiO_2	4.67	7.49
0.57% K_2O + 0.75% SiO_2	5.33	10.90
Equilibrium	5.86	16.43

† From P. H. Emmett, "Fixed Nitrogen," H. A. Curtis, editor, Chemical Catalog Company, Inc., New York, 1932.

to avoid a serious reduction in activity. With pure 3:1 hydrogen-nitrogen gas, operation for 7 to 8 years has been reported.

Manufacture. The production of a catalyst containing about 66 per cent Fe_2O_3 , 31 per cent FeO , 1.0 per cent K_2O , and 1.8 per cent Al_2O_3 has been described.²⁸ "The process consists of (1) purification of high grade natural magnetite ore by dry tabling on an air separator table, (2) preparation of synthetic magnetite by burning high-purity ingot iron in oxygen, and (3) fusion of a mixture of synthetic magnetite, purified natural magnetite, ingot iron, potassium nitrate, aluminum oxide, and recycled catalyst fines, followed by sizing of the fused product by crushing, tumbling, and screening." The ferrous and ferric iron oxides were held near the preferred mole ratio of 1:1, and impurities such as sulfur and phosphorus were kept to a minimum. The synthetic magnetite was prepared in an iron-oxidation unit. Fourteen iron rods were fed continuously to this unit at the same time and burned in an atmosphere of oxygen. The fused synthetic magnetite collected in a pot and solidified. It was later crushed for use in a catalyst-fusion furnace.

The ingredients of the catalyst, including the promoters, were fused in the electric-resistance catalyst-fusion furnace. These ingredients were placed on a bed of refractory lining, similar in composition to the material being fused, in horizontal fusion shells. These were 11 ft long and semicircular in cross section, 12 in. deep, and 24 in. wide. Hoods were provided to remove the nitrogen oxide fumes evolved during the fusion. The mixture was distributed evenly along a taut handmade wire chain and formed a mound extending above the top of the shell. The chain was stretched between the electrodes and served to generate sufficient heat, in carrying

²⁸ G. L. Bridger, G. R. Pole, A. W. Beinlich, Jr., and H. L. Thompson, *Chem. Eng. Progr.*, **43**:291 (1947).

the initial current, to produce a continuous molten core of oxide before melting itself. This core was conductive enough to carry the current thereafter. A potential of 220 volts was applied to the chain, and this was gradually decreased during the first hour to about 35 volts and was then held constant. The initial charge shrank on melting, and additional mixture was added over a 3-hr period. After all the charge was added, the current reached a constant value of about 4,000 amp, and this was maintained for 1 hr after all the material melted to allow for thorough mixing. The melt was solidified, crushed, and sized with the $-3 + 6$ mesh fraction being used as catalyst. The bulk density of the catalyst was 155 to 160 lb/cu ft. The catalyst was appreciably hygroscopic because of its potash content, and it became visibly wet on standing in the atmosphere.

Activation. The activity of the catalyst is influenced by the activation schedule followed after it is placed in the reactor. The activation consists in reducing the iron oxides to the metallic state with the purified hydrogen-nitrogen synthesis-gas mixture. The promoters remain as oxides after activation. In a suitable activation schedule²⁸ in a laboratory reactor, the catalyst was reduced at 100 atm and at a space velocity of 5,000 during the first half of the schedule, and at a space velocity of 10,000 in the second half. Reduction required 70 hr, during which time the catalyst was heated at a substantially constant rate from room temperature to 450°C with 5-hr heating arrests at about 260 and 340°C. Activation is completed when the evolution of water ceases and conversion to ammonia becomes steady.

Poisons. The action of temporary and permanent poisons is considered in Chap. 11. Compounds which act as permanent poisons to iron catalysts include sulfur, selenium, tellurium, phosphorus, arsenic, boron, hydrogen sulfide, and sulfur dioxide. The temporary poisons include oxygen, water vapor, carbon dioxide, and carbon monoxide. The temporary nature of the poisoning by a small percentage of water vapor is shown in Fig. 11-7. The catalyst was operated normally on a dry gas, and then water vapor was introduced continuously to the extent of only 0.32 per cent of the entering gas. This caused a very marked reduction in the per cent of ammonia in the gas leaving the catalyst. When the water vapor was shut off, the per cent ammonia returned to very nearly its original figure. Excessive quantities of temporary poisons lead to permanent impairment of the activity of the catalyst.

12-7. Synthesis Reactor. The synthesis reactor or converter is designed to carry out the reaction between hydrogen and nitrogen. The equipment for gas production, purification, and compression has been provided to prepare the gas for this key step in the process. Hein²⁹ describes five converters designed for operation at 350 atm or less as follows:

²⁹ L. B. Hein, *Chem. Eng. Progr.*, **48**:412 (1952).

The most important factors in the design of a converter are the arrangement of heat exchangers so that gas is made to flow through the converter in such a way as to maintain an optimum catalyst temperature, design such that no sudden changes in temperature occur anywhere, and the use of construction materials capable of withstanding pressures, high temperature, and chemical attack.

Temperature control is extremely important because the attainment of a reaction rate high enough to make the process economically feasible requires operation at a temperature near that at which catalyst deactivation becomes rapid and materials are attacked at an appreciable rate. Heat released from the synthesis reaction is not uniform throughout the catalyst bed and hence there is a tendency toward localized overheating. Furthermore, the "hot spot" is shifted through changes in the conditions of operation and through aging of the catalyst. Therefore, in the ideal converter, it is desirable to control the removal of heat at each point in the converter. Such a converter has not been developed but there are converters that approach this ideal arrangement. In other converters the heat exchangers and the flow of gas are arranged to minimize the temperature difference in the catalyst that is caused by the heat of reaction.

Alloyed tubes are used in the heat exchangers of modern converters. The arrangement is such that the exchanger tubes, which operate at high temperatures, are not required to withstand pressure differentials and the converter shell, which has synthesis pressure on one side and atmospheric pressure on the other, is kept at a low temperature to prevent weakening of metal.

Shell temperatures are kept low by the flow of cool gases next to and inside the shell and through use of an insulating material between the cool gases and the internals of the converter.

Ammonia synthesis converters may be considered to be of two types. One type employs layers of catalyst with means for cooling the gases between layers. This type, in which the temperature of the gas is controlled at various levels in the converter, is an approach to point-by-point temperature control and is exemplified by the Fauser-Montecatini converter as shown in [Fig. 12-8] and by the converter designed by the M. W. Kellogg Co. as shown in [Fig. 12-9]. The Nitrogen Engineering Corp., Tennessee Valley Authority, and Mont Ceniz processes employ converters in which gas flow and heat exchangers are arranged to minimize temperature difference in the catalyst. The NEC converter is shown in [Fig. 12-10]. The TVA-type converter as designed by C. O. Brown for the TVA is shown in [Fig. 12-11].

Fauser-Montecatini Converter. The most recent modification of the Fauser-Montecatini converter [Fig. 12-8] is unique in that steam is produced from surplus heat generated by the synthesis reaction. Synthesis gas enters the converter at (13), passes through the shell side of heat exchanger (7), flows upward in the annular space between the converter shell and catalyst basket, downward over the layers of catalyst (1-6), and through the exchanger tubes (7) to the converter outlet. The temperature of the gas during its upward and downward flow and its ammonia content also are given in the figure. Feed water enters an economizer (8), which may or may not be used, passes to flash chamber (11), through a circulation pump (10), through the converter shell to coils (17) in the converter, and through the converter shell (12) back to the

flash chamber. Valves (9) are used to control the rate of water flow through the coils at various levels and thereby control the temperature in the converter

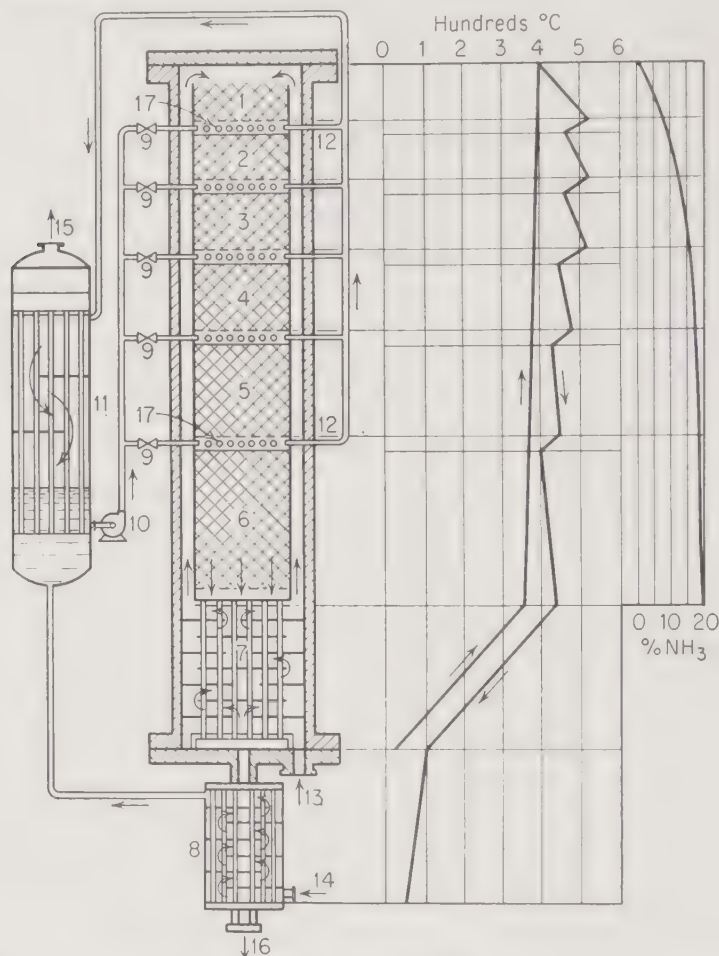


FIG. 12-8. Ammonia-synthesis converter used in Fauser-Montecatini process. [From L. B. Hein, *Chem. Eng. Progr.*, **48**:412 (1952), Montecatini Company.]

The following data are said to apply to the Fauser-Montecatini converter:

Working pressure, atm.....	300
Ammonia production, tons NH_3 /day.....	55
Ammonia content of gas, %	
Inlet to converter.....	1.5
Outlet from converter.....	20.0
Temperature of gas, °C.	
Inlet to converter.....	20
Outlet from converter.....	100
Steam production, 150 lb./sq. in. gage, 250°C.	
lb. steam	
lb. NH_3 produced.....	0.8

Advantages claimed for the converter are (1) increased thermal efficiency to produce steam from surplus heat and (2) improved control of catalyst temper-

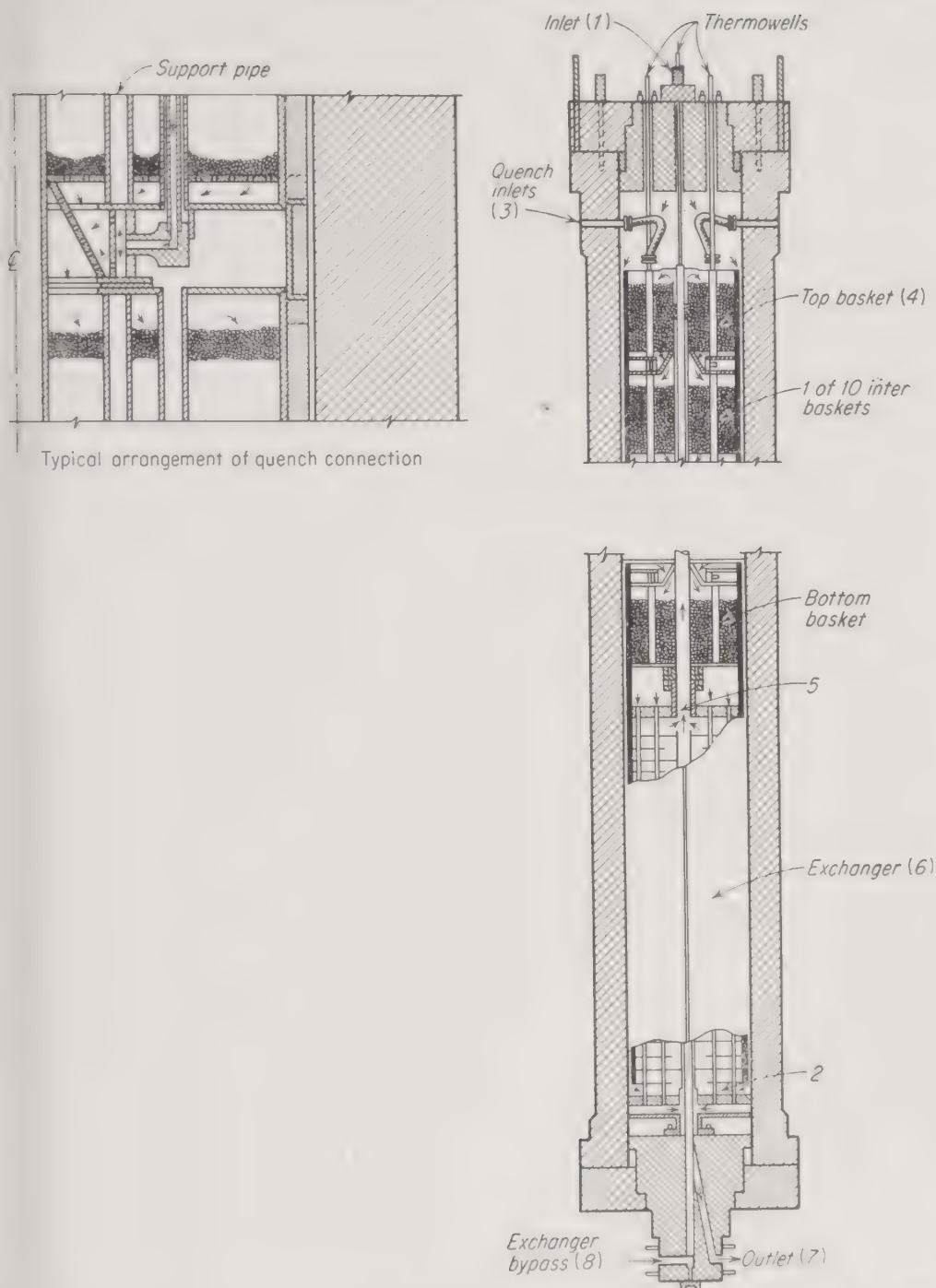


FIG. 12-9. Ammonia-synthesis converter used in Kellogg process. [From L. B. Hein, *Chem. Eng. Progr.*, **48**:412 (1952), Commercial Solvents Corporation.]

ature to increase ammonia production capacity and decrease power consumption for gas circulation.

Montecatini has recently installed this type converter at its Merano and Novara works in Italy. (Information on the converter was supplied by the Montecatini Co., Milano, Italy.)

Kellogg Converter. In the Kellogg converter [Fig. 12-9] gas enters the converter at (1), passes down the annular space between the shell and internals of the converter to the bottom of the heat exchanger (2), upward through the

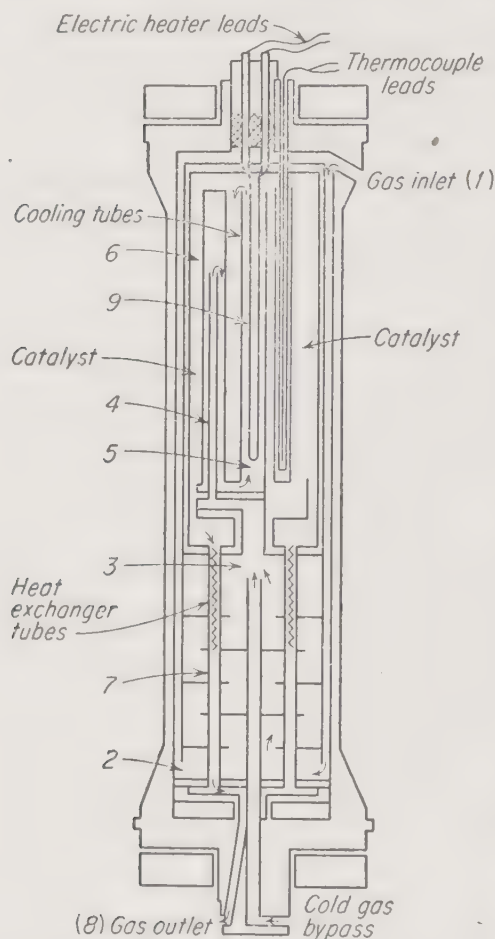


FIG. 12-10. Ammonia-synthesis converter used in Nitrogen Engineering Corporation process. [From L. B. Hein, *Chem. Eng. Progr.*, **48**:412 (1952), Chemical Construction Company.]

(1), flows downward through the annular space next to the outside shell and enters the bottom of the heat-exchanger section (2) outside the tubes. Near the top of the heat exchanger (3) the gas is mixed with cold by-pass gas in such proportion as to give the desired operating temperature in the catalyst.

The cooling tubes (4) in the catalyst basket are of double pipe sections. Gas flows upward through the inner pipes, downward through the annular spaces to

shell side of the heat exchanger (6) through center pipe of the catalyst basket (5), downward over the layers of catalyst (4), and through the heat exchanger tubes to outlet (7). Gases for control of temperature by quenching between catalyst layers enter at (3). The degree of preheat of the gas to the top of the catalyst is controlled by the by-passing of a portion of the inlet gas around the heat exchanger. The inlet for the by-pass gas is at the bottom of the converter at (8).

The converter operates at about 350 atm., and 80 cu. ft. of catalyst is employed. The converter is operated to produce 100 tons of ammonia per day. Catalyst life experienced in this converter has been about four years. (Information on the converter was supplied by Commercial Solvents Corp.)

NEC Converter. The NEC converter [Fig. 12-10] is an example of the type in which temperature differences in the catalyst are minimized by the arrangement of heat exchangers and gas flow. This converter is designed by the Chemical Construction Corp.

The converter consists of a heat exchanger in the lower section and a catalyst basket with cooling tubes in the upper section. The main gas flow enters near the top of the converter at

a header, upward again through a collecting tube (5), downward through the catalyst outside the tubes (6), and then through the heat-exchanger tubes (7) to the converter outlet (8). Heat exchange to control catalyst temperature is between gases inside and outside the cooling tubes in cocurrent flow.

The converter is fabricated in two sizes of 700 and 800 mm. diam. The smaller one contains 53 cu. ft. of catalyst and the larger one contains 70 cu. ft. At 350 atm. these converters will produce from 1.5 to 1.9 tons of ammonia/(cu. ft. of catalyst)(day) depending on the concentration of inerts in the recycle gas, temperature of cooling water, and amount of refrigeration employed in the process.

An electric heater (9), located in the gas-collecting tube (5), is provided for heating the gas used to preheat the converter. The heater also may be used to control the temperature of the gas entering the catalyst. It is claimed that the heater usually has a life equal to that of the inside metal parts of the converter. (Information on the converter was supplied by the Chemical Construction Corp.)

TVA Converter. This converter also is designed for gas flow and heat exchange to minimize temperature differences in the catalyst [Fig. 12-11]. The main flow of synthesis gas enters the bottom of the converter at (1) and is preheated by countercurrent heat exchange (2) with hot gas flowing downward from the catalyst. Gas leaves the converter at the bottom (5). Synthesis gas for cooling the outside shell of the converter enters the top (3), passes down the converter through the annular space next to the shell, and mixes with the main gas flow at the base of the exchanger. Gas that is by-passed around the exchanger to control catalyst temperature enters the bottom of the converter at (4) and mixes with the remainder of the synthesis gas in the upper part of the heat exchanger.

The converter, which contains 144 cu. ft. of catalyst, is operated at a pressure of from 250 to 350 atm. The amount of catalyst in this converter exceeds the

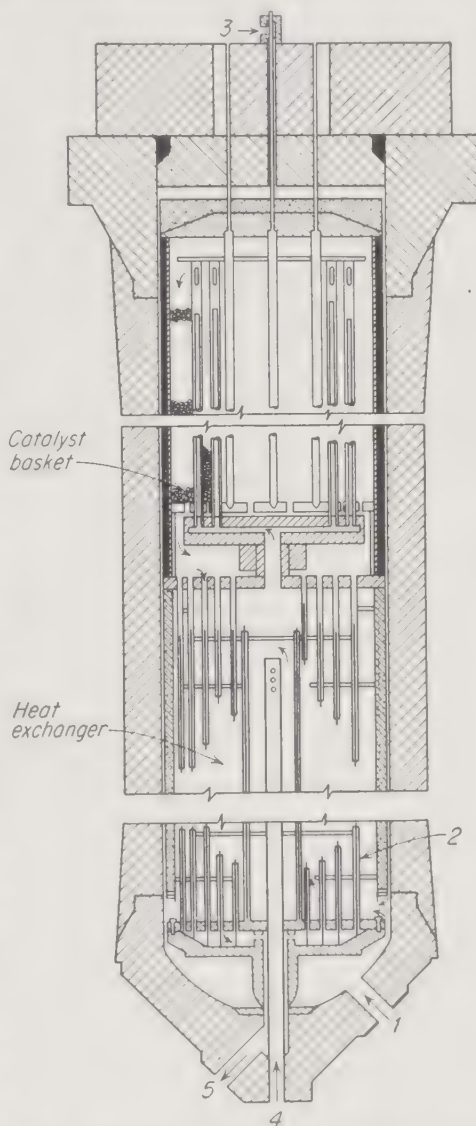


FIG. 12-11. Ammonia-synthesis converter used in TVA process. [From L. B. Hein, *Chem. Eng. Progr.*, **48**:412 (1952).]

presently installed capacity for compressing synthesis gas. Ammonia production from this converter is about 140 tons per day.

Aside from structural differences between this converter and the NEC converter, heat transfer in the TVA catalyst basket is accomplished through counter-current flow of gas whereas in the NEC catalyst basket the flow is cocurrent. Considerable controversy has existed among designers as to whether counter-current or cocurrent gas flow in the converter is more effective in maintaining optimum temperatures throughout the catalyst. Calculations indicate that at normal operating conditions the mean-temperature difference between gas inside the tubes and that passing through the catalyst is about the same for either type of flow. Satisfactory control of catalyst temperature by either method is indicated by the fact that both types of converters have given efficient operation for prolonged periods.

A gas-fired heater located outside the converter is used for heating the synthesis gas with which the TVA converter is brought to operating temperature. Because of the time required to place the heater in operation, heat from this source cannot be supplied quickly to supplement heat of reaction as is desirable occasionally.

Mont Cenis Converter. The converter used in the Mont Cenis process, which operates at about 160 atm., also is designed to minimize temperature differences in the catalyst. Preheated gas from heat exchangers located outside the synthesis converter enters the converter at the bottom and travels upward in the space between the shell of the converter and catalyst basket. The gas is heated further by passing through tubes in the catalyst bed. The gas flows downward through the inner of two concentric tubes, then upward through the annular space between the tubes, and out to the top of the catalyst bed. The tubes extend downward the length of the catalyst bed. From the tubes the gas flows downward through the catalyst and leaves through the bottom of the converter.

The converter is charged with 16 tons of catalyst and is capable of producing 200 tons of ammonia per day when operated at 20,000 space velocity. The life of the catalyst in this converter is reported to be about four years. [Information on the converter was supplied by the Shell Chemical Corp.]

Claude Converter. Thompson, Guillaumeron, and Updegraff³⁰ describe the present-day Claude³¹ converter for operation at 1,000 atm as follows:

Essential details of the Claude-converter design are illustrated in [Fig. 12-12] which is a diagrammatic sketch of an ammonia converter cross section. The methanation converter is similar in design.

The converter shell is a thick-walled carbon steel cylinder with top and bottom closures. A basket, or cartridge, containing heat-exchange tubes and catalyst fits inside the shell, occupying most of its length. Electric heating coils for start-up and temperature control also are part of the cartridge assembly. The

³⁰ H. L. Thompson, Pierre Guillaumeron, and N. C. Updegraff, *Chem. Eng. Progr.*, **48**:468 (1952).

³¹ G. Claude, *Trans. Faraday Soc.*, **18**:219 (1922); *Ind. Eng. Chem.*, **14**:1118 (1922); *Engineering*, **114**:506 (1922).

cartridge is an integral unit which may be lifted from the shell by removing the top closure and breaking minor connections at the bottom.

The main stream of incoming cold gas enters through an opening in the bottom closure, passes around the closed bottom of the cartridge and upward through a narrow annulus between the shell and the cartridge wall, which is wrapped on the outside with an insulating material. The cold gas controls the shell wall

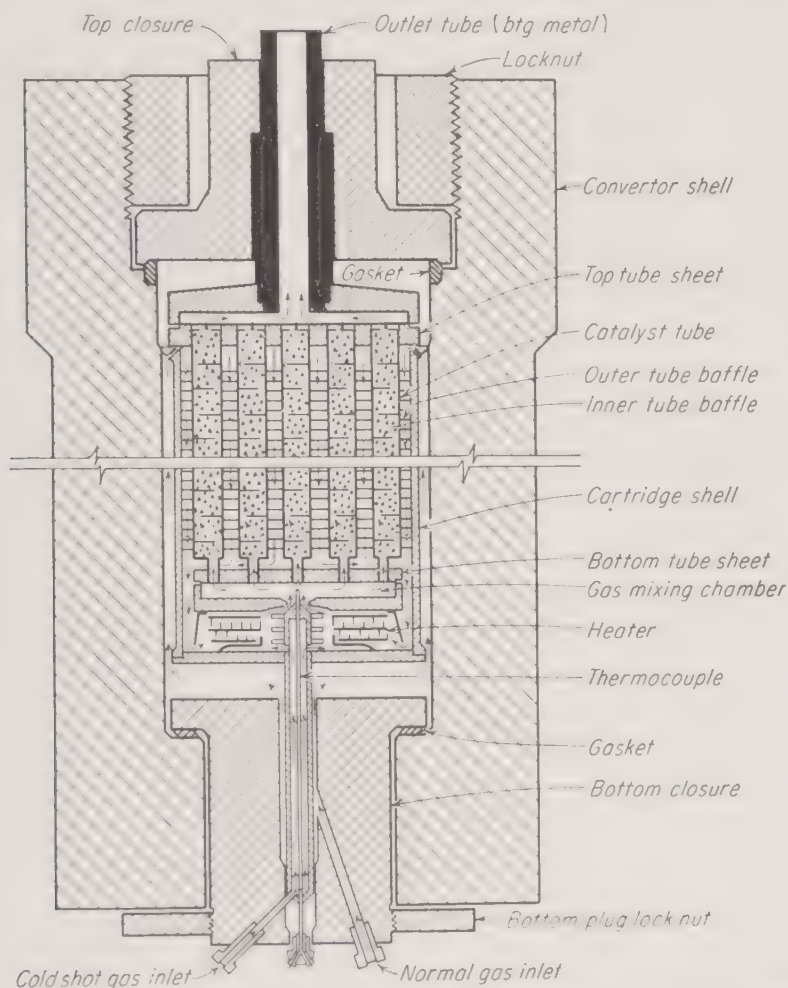


FIG. 12-12. Ammonia-synthesis converter used in the Claude process. [From H. L. Thompson, P. Guillaumeron, and N. C. Updegraff, *Chem. Eng. Progr.*, **48**:468 (1952).]

temperature, so that it ordinarily does not exceed 120°F. This gas enters the body of the cartridge through radial holes drilled in the cartridge wall at the top. The catalyst tubes are closely spaced in concentric circles inside the cartridge. These tubes are open at the top, where they are attached to the tube sheet. The tubes are plugged at the bottom and each plug is drilled to take an adapter nipple of smaller bore than the tube. The adapter thus projects downward from the plug. These adapters fit into a bottom tube sheet, whose outside diameter is slightly less than the inside diameter of the cartridge wall, so that

space is left for downward flow of gas around the bottom tube sheet. A short gas-mixing chamber is provided just below the bottom tube sheet.

Full-disk baffles drilled to fit snugly around the outside of the tubes direct the downward flow of fresh cold gas entering at the top of the cartridge. Small slots are cut through the baffles at the periphery of the tube walls and the gas passes downward through these slots. The slot positions are staggered from baffle to baffle and the gas thus is forced into highly turbulent flow which is concentrated at the tube walls. Preheated gas passing through the bottom baffle goes around the bottom tube sheet and into the gas-mixing chamber where it meets a by-pass stream of (usually) cold gas.

The freshly converted gas rising from the catalyst hot zone loses heat to the incoming cold gas; by the time it leaves the tubes its temperature has been reduced so that its sensible heat gain closely approximates the heat of reaction. The operation therefore is essentially autothermal. The necessary outlet gas temperature for autothermal operation is readily calculable from knowledge of recirculation rates and ammonia concentrations, and this outlet temperature is an important control point. The thermocouple in the gas-mixing chamber, which measures temperature of the inlet gas mixture, also is important in controlling the operation. The upward gas flow through the catalyst is directed by circular segmental baffles which are inserted as the catalyst is charged into the tubes.

The gas issuing from the top of the catalyst tubes is collected in a cover over the top tube sheet, whence it passes through the outlet tube to the precooler shown in [Fig. 12-7]. The outlet tube and a short length of piping up to the cooler are made of BTG metal, which is an alloy of nickel, chromium and iron with some tungsten. BTG metal is particularly adapted to withstanding hydrogen attack at high pressure and elevated temperatures. Its yield point remains high at elevated temperatures. In the present Claude design it is used only where the combination of high pressure and temperature is unavoidable. The only pieces of BTG equipment besides those just named are the tube bottom plugs and the thermocouple well.

Each converter contains about 16.5 cu ft of catalyst and the space velocity in the two converters shown in Fig. 12-7 is 44,000 in the first and 30,000 in the second. The space-time yield in the two converters is 410 and 245 respectively, expressed as pounds of ammonia synthesized per hour per cubic foot of catalyst. These may be compared with values for a synthesis system operating at about 285 atmospheres and a catalyst temperature of about 930°F where the space velocity was reported as 9,000 to 11,000 and the space-time yield as about 48.

12-8. Kinetics of the Reactor. The rate of the synthesis reaction in the presence of a catalyst can be related to the idealized concept of the mechanism of the reaction. This is a theoretical approach to the kinetics of the reaction. The rate of reaction has also been measured, and these measurements may be compared with the predictions derived from the theory or they may be used directly to interpret the kinetics of the reaction for the purpose of designing a reactor.

Low-pressure Isothermal Theory. Temkin and Pyzhev³² have offered an explanation of the kinetics of this reaction. Experiments have shown that one step in the reaction controls the rate of formation of ammonia. This step is the adsorption of nitrogen on the active centers of the catalyst. Nitrogen is activatedly adsorbed and forms an activated complex with the catalyst. The activated nitrogen reacts rapidly with hydrogen to form ammonia. The activated nitrogen and gaseous hydrogen and ammonia on or in contact with the surface are in chemical equilibrium. At moderate pressures where the perfect-gas law is valid, the following relations exist.

For the over-all reaction



For the nitrogen adsorption which is the rate-controlling step



For the reaction which proceeds rapidly to equilibrium



The adsorption step at equilibrium is governed by the equation

$$\theta = \frac{1}{s} \ln bP_{\text{N}_2} \quad (12-18)$$

Adsorption equilibrium is approached at a rate given by the rate-of-adsorption equation

$$R_a = k_a p_{\text{N}_2} e^{-\theta} \quad (12-19)$$

The adsorption of nitrogen is reversible, and nitrogen is desorbed from the surface at a rate given by the desorption equation

$$R_d = k_d e^{h\theta} \quad (12-20)$$

The constants are related by the equations

$$\frac{g}{s} = \alpha \quad \frac{h}{s} = \beta \quad \alpha + \beta = 1 \quad (12-21)$$

The activated nitrogen on the catalyst surface is in chemical equilibrium with hydrogen and ammonia in the gas in contact with the surface. The nitrogen-gas pressure which would be in adsorption equilibrium with the activated nitrogen on the surface is P_{N_2} and is given by the equation

$$P_{\text{N}_2} = \frac{p_{\text{NH}_3}^2}{K_p p_{\text{H}_2}^3} \quad (12-22)$$

³² M. Temkin and V. Pyzhev, *Acta Physicochim. U.R.S.S.*, **12**:327 (1940).

Then the fraction of the surface which is covered is

$$\theta = \frac{1}{s} \ln \frac{b p_{\text{NH}_3}^2}{K_p^2 p_{\text{H}_2}^3} \quad (12-23)$$

and, substituting this value of θ in Eq. (12-19), the rate of nitrogen adsorption is

$$\begin{aligned} R_a &= k_a p_{\text{N}_2} \exp \left[- \frac{g \ln \left(\frac{b}{K_p^2} \frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}^3} \right)}{s} \right] \\ &= k_1 p_{\text{N}_2} \left(\frac{K_p^2 p_{\text{H}_2}^3}{b p_{\text{NH}_3}^2} \right)^\alpha = k_1 \frac{p_{\text{N}_2} p_{\text{H}_2}^{1.5}}{p_{\text{NH}_3}} \left(\frac{K_p^2}{b} \right)^{0.5} \end{aligned} \quad (12-24)$$

since experimental data indicate that $\alpha = 1/2$. The rate of desorption is found in a similar fashion to be

$$R_d = k_d \exp \left[\frac{h \ln \left(\frac{b}{K_p^2} \frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}^3} \right)}{s} \right] = k_2 \left(\frac{p_{\text{NH}_3}^2 b}{p_{\text{H}_2}^3 K_p^2} \right)^{0.5} \quad (12-25)$$

The net rate of synthesis is the difference between the forward and reverse reactions and as expressed by Emmett and Kummer³³ is given by

$$\begin{aligned} \rho_B W (R_a - R_d) &= \frac{1}{2} \frac{dN_{\text{NH}_3}}{dt} = k_1 W \rho_B \frac{p_{\text{N}_2} p_{\text{H}_2}^{1.5}}{p_{\text{NH}_3} (b/K_p^2)^{0.5}} \\ &\quad - \frac{k_2 \rho_B W p_{\text{NH}_3} (b/K_p^2)^{0.5}}{p_{\text{H}_2}^{1.5}} \end{aligned} \quad (12-26)$$

where N_{NH_3} is moles of ammonia in catalyst volume W . At equilibrium $dN_{\text{NH}_3}/dt = 0$, and consequently

$$\frac{b}{K_p^2} \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{k_1}{k_2} = b \quad (12-27)$$

or for convenience

$$\frac{k_1}{b^{1/2}} = k_2 b^{1/2} = f \quad (12-28)$$

Combining Eqs. (12-28) and (12-26),

$$\frac{dN_{\text{NH}_3}}{dt} = 2f W \rho_B \left(\frac{p_{\text{N}_2} p_{\text{H}_2}^{1.5} K_p}{p_{\text{NH}_3}} - \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{1.5} K_p} \right) \quad (12-29)$$

The mole fractions of nitrogen, hydrogen, and ammonia may be expressed in terms of the volume fraction of ammonia in the gas Z . After ammonia

³³ P. H. Emmett and J. T. Kummer, *Ind. Eng. Chem.*, **35**:677 (1943).

has been formed from a 3 hydrogen to 1 nitrogen initial mixture, the mole fraction n of each component is

$$\begin{aligned} n_{\text{NH}_3} &= Z \\ n_{\text{H}_2} &= \frac{3}{4}(1 - Z) \\ n_{\text{N}_2} &= \frac{1}{4}(1 - Z) \end{aligned} \quad (12-30)$$

With steady flow through a catalyst bed, let N_0 be the moles of hydrogen-nitrogen mixture equivalent to the mixture of hydrogen-nitrogen-ammonia in the volume of catalyst W . The moles of ammonia in the mixture will be N_{NH_3} , and the total moles will be $N_0 - N_{\text{NH}_3}$, since each mole of ammonia was formed from 2 moles of hydrogen-nitrogen mixture. Then .

$$Z = \frac{N_{\text{NH}_3}}{N_0 - N_{\text{NH}_3}} \quad (12-31)$$

and

$$dN_{\text{NH}_3} = N_0 \frac{dZ}{(1 + Z)^2} \quad (12-32)$$

For the pressure range where the perfect-gas law applies, Eq. (12-29) may be written as

$$\begin{aligned} & \frac{2fW\rho_B}{N_0 p^{0.5}} \frac{dt}{dZ} \\ &= \frac{1}{(1 + Z)^2} \left[\frac{K_p p^{2\frac{1}{4}} (\frac{3}{4})^{1.5} (1 - Z)^{2.5}}{Z} - \frac{Z}{(\frac{3}{4})^{1.5} (1 - Z)^{1.5} K_p} \right] \end{aligned} \quad (12-33)$$

Also

$$N_0 = \frac{\varphi p (1 + Z) W}{RT} \quad (12-34)$$

The time of contact between the gas and the catalyst is $273RN_0/U_0$, and, if the volume of catalyst is increased by an infinitely small amount dW , the resultant increase in contact time is

$$dt = \frac{273p\varphi(1 + Z)}{U_0 T} dW \quad (12-35)$$

and also

$$d\left(\frac{1}{V_0}\right) = \frac{dW}{U_0} \quad (12-36)$$

Combining Eqs. (12-33) to (12-36),

$$\begin{aligned} & \frac{546Rf\rho_B}{p^{0.5}} \int d\left(\frac{1}{V_0}\right) \\ &= \int \frac{1}{(1 + Z)^2} \left[\frac{K_p p^{2\frac{1}{4}} (\frac{3}{4})^{1.5} (1 - Z)^{2.5}}{Z} - \frac{Z}{(\frac{3}{4})^{1.5} (1 - Z)^{1.5} K_p} \right] dZ \end{aligned} \quad (12-37)$$

A modification of this equation for use at higher pressure is given in the next section. The equation may be integrated graphically and used to evaluate the constant f from measurements in an isothermal reactor.

High-pressure Isothermal Theory. The Temkin and Pyzhev³² equations were derived for isothermal conditions with a perfect gas and should be modified for pressures above 100 atm, where considerable deviations from the perfect-gas law occur. To do this the derivation for low pressures is changed to include the fugacity of the gases and the fugacity coefficients. It is to be recalled that the controlling step in the sequence of steps which convert hydrogen and nitrogen to ammonia is the adsorption of nitrogen on the catalyst. For this step to proceed, there must be an appreciable difference between the partial pressure of nitrogen in the main body of the gas (or in the gas at the catalyst surface) and the partial pressure which would be in equilibrium with the nitrogen adsorbed on the surface of the catalyst. These two partial pressures of nitrogen will be represented by p_{N_2} and P_{N_2} , respectively. Once adsorbed on the catalyst, the nitrogen reacts quickly to form ammonia, with the result that adsorbed nitrogen, hydrogen, and ammonia are very nearly in chemical equilibrium. Both hydrogen and ammonia are also adsorbed on the catalyst surface, but the partial pressure of these in adsorption equilibrium with the catalyst surface is the same as the partial pressure in the main body of the gas (when the resistance to mass transfer between the surface and main body is negligible), so no distinction between the two partial pressures need be made. The chemical equilibrium for Eq. (12-15) on the catalyst surface is represented by

$$K = \frac{\bar{f}_{NH_3}}{\bar{f}_{H_2}^{3/2} \bar{f}_{N_2}^{1/2}} \quad (12-38)$$

where $\bar{f}_{N_2}^*$ is the fugacity of nitrogen gas when in equilibrium with nitrogen adsorbed on the catalyst surface. The fugacity may be expressed as $\bar{f}_A = \bar{\phi}_A p y_A$ according to Eq. (8-125). At pressures up to 300 atm the fugacity may be determined by the Lewis and Randall fugacity rule according to Eq. (10-28). At higher pressures, this rule leads to increasingly larger errors.³⁴ The methods described in Chap. 8 may be used at higher pressures. Since $p y_{N_2}^* = P_{N_2}$, in general $\bar{f}_{N_2}^* = \bar{\phi}_{N_2}^* P_{N_2}$, and

$$K = \frac{y_{NH_3} p \bar{\phi}_{NH_3}}{y_{H_2}^{3/2} p^{3/2} \bar{\phi}_{H_2}^{3/2} P_{N_2}^{1/2} \bar{\phi}_{N_2}^{1/2}} = \frac{y_{NH_3} K_\phi^*}{y_{H_2}^{3/2} p^{1/2} P_{N_2}^{1/2}} \quad (12-39)$$

and therefore

$$P_{N_2} = \frac{y_{NH_3}^2 K_\phi^{*2}}{y_{H_2}^3 p K^2} \quad (12-40)$$

³⁴ S. Glasstone, "Thermodynamics for Chemists," p. 277, D. Van Nostrand Company, Inc., New York, 1947.

The value of P_{N_2} is the partial pressure of nitrogen at adsorption equilibrium and may be substituted in Eq. (12-18) and in the adsorption-rate equation (12-19) and the desorption-rate equation (12-20), leading to the following equation for the net rate of ammonia synthesis. K_ϕ^* is evaluated at the concentration of hydrogen and ammonia in the gas and at the concentration of nitrogen in equilibrium with the catalyst surface.

$$\begin{aligned} W(R_a - R_d) &= \frac{1}{2} \frac{dN_{NH_3}}{dt} \\ &= k_a W y_{N_2} p (b K_\phi^{*2} / p K^2)^{-0.5} \frac{y_{H_2}^{1.5}}{y_{NH_3}} \\ &\quad - k_d \rho_B W \left(\frac{b K_\phi^{*2}}{p K^2} \right)^{0.5} \frac{y_{NH_3}}{y_{H_2}^{1.5}} \quad (12-41) \end{aligned}$$

At equilibrium the rate of ammonia synthesis is zero, and by equating the two terms on the right of Eq. (12-41)

$$k_a = k_d \frac{b K_\phi^{*2}}{p^2 K^2} \frac{y_{NH_3}^2}{y_{H_2}^3 y_{N_2}} = k_d b \quad (12-42)$$

For convenience this may be written

$$\frac{k_a}{b^{0.5}} = k_d b^{0.5} = k' \quad (12-43)$$

For a mixture which initially contained a ratio of 3 moles of hydrogen to 1 mole of nitrogen, Eq. (12-34) becomes

$$N_0 = \frac{\varphi p (1 + Z) W}{z R T} \quad (12-44)$$

and Eq. (12-35) becomes

$$dt = \frac{273 z_s p \varphi (1 + Z)}{z U_0 T} dW \quad (12-45)$$

where the compressibility factors z and z_s (at standard conditions) have been introduced to correct for deviations from the perfect-gas laws. Equations (12-30), (12-32), (12-36), (12-41), (12-43), (12-44), and (12-45) may be combined to give

$$d \left(\frac{1}{V_0} \right) = \frac{(p^{0.5} / 546 k' R z_s \rho_B) dZ}{(1 + Z)^2 \left[\frac{1_4 (3_4)^{1.5} (1 - Z)^{2.5} p^2}{Z (K_\phi^* / K)} - \frac{Z (K_\phi^* / K)}{(3_4)^{1.5} (1 - Z)^{1.5}} \right]} \quad (12-46)$$

Rearranging and integrating,

$$\begin{aligned} \frac{1}{V_0} &= 546 k' R z_s \rho_B \\ &= V_0 p^{0.5} \int_0^Z \frac{Z (3_4)^{1.5} (1 - Z)^{1.5} dZ}{(1 + Z)^2 \left[\frac{1_4 (3_4)^3 (1 - Z)^4 p^2 (K / K_\phi^*)}{Z} - Z^2 (K_\phi^* / K) \right]} \quad (12-47) \end{aligned}$$

TABLE 12-4. REACTION-RATE CONSTANT f' EVALUATED BY EQ. (12-47)[†]

p , atm	V_0 , hr ⁻¹	350°C	400°C	450°C	475°C	500°C	400°C	450°C	475°C	400°C	450°C	475°C
100	25,000	1.25	11.7	39.1	76.0	114						
	50,000	1.02	12.8	52.9	100	145						
	75,000	0.61	12.5	61.4	113	155						
	100,000	0.50	10.3	66.8	117	175						
200	25,000	0.65	6.65	31.4	59.0	87.2	6.33	20.7	33.2	11.2	21.2	34.1
	50,000	0.51	5.67	42.3	76.3	120	6.15	22.4	38.4	9.9	24.9	46.1
	75,000	0.25	4.80	45.5	85.2	131	6.18	23.8	41.5	11.1	29.8	47.0
	100,000	0.14	4.02	44.5	85.1	138	6.15	25.2	47.4	10.9	35.3	56.2
300	25,000	0.51	5.61	20.7	55.0	51.8						
	50,000	0.11	4.11	26.8	61.2	67.4						
	75,000	0.06	3.49	26.3	56.2	77.3						
	100,000	0.04	2.83	23.5	42.0	76.6						

[†] From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953), corrected.

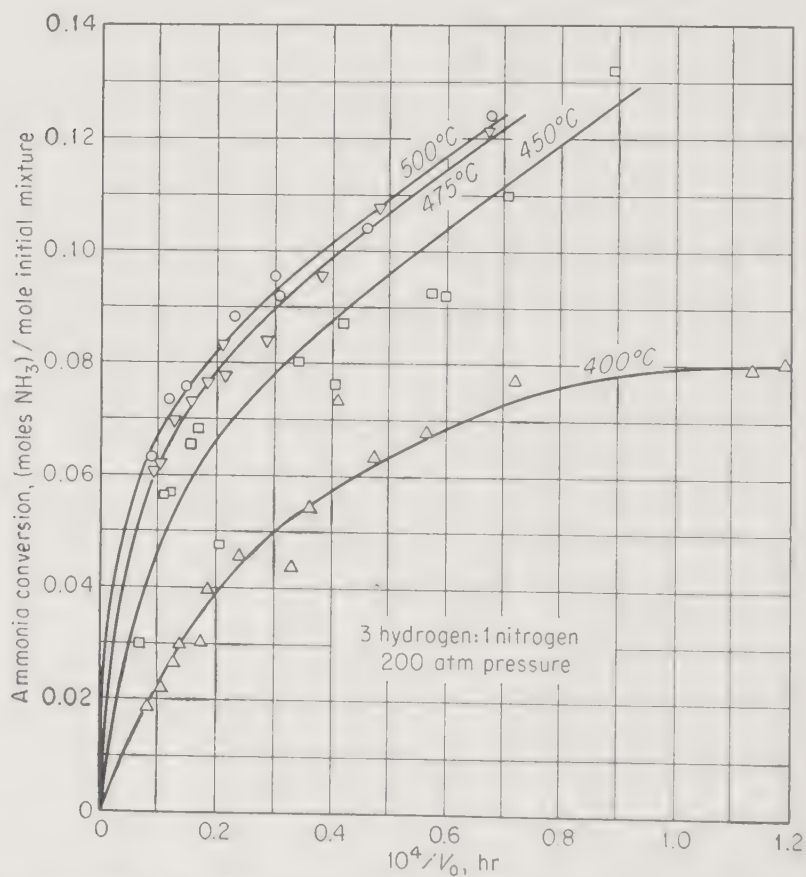


FIG. 12-13. Fractional conversion to ammonia vs. the reciprocal of the space velocity at 200 atm. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

Measured Rates. The per cent ammonia was determined in the exit gas from an experimental reactor by Adams and Comings.¹¹ This reactor was described in Chap. 7 and Fig. 7-30. Measurements were made over a range of space velocities, at five temperatures, three pressures, and with

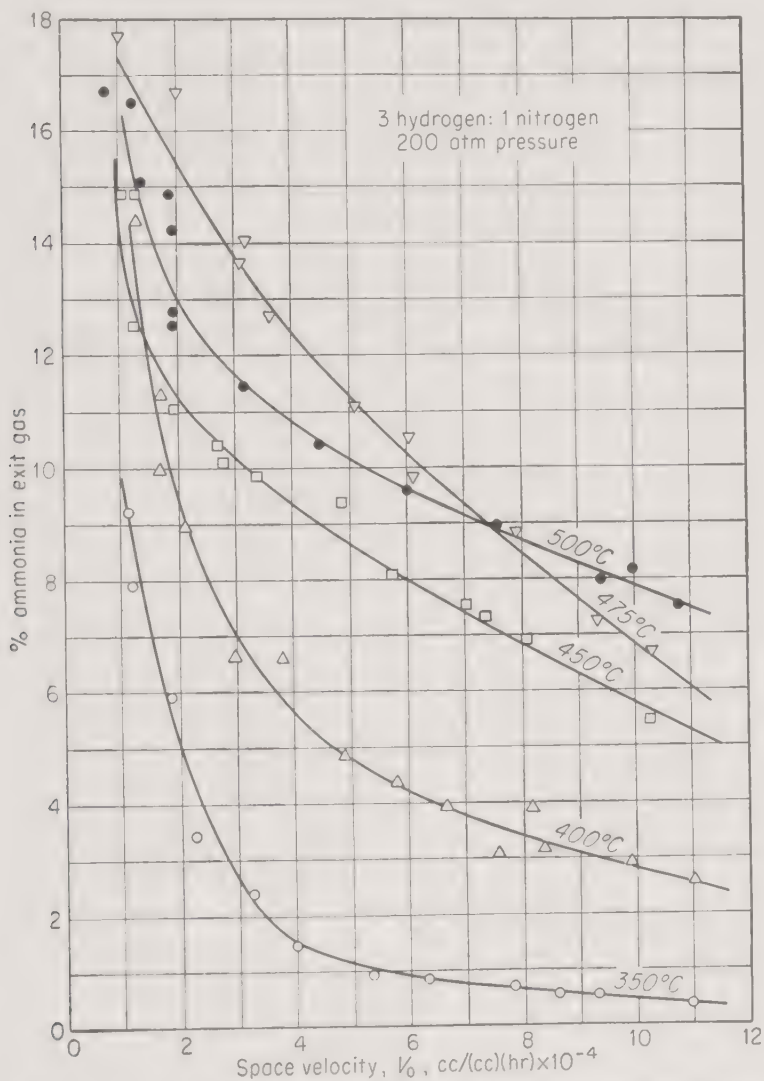


FIG. 12-14. Per cent ammonia in the exit gas vs. space velocity at 200 atm. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

three ratios of hydrogen to nitrogen in the feed gas. The results were used to calculate values of f' , and these are listed in Table 12-4. The data may also be used directly to determine the rate of ammonia formation as a function of temperature and per cent ammonia in the gas. This is done by a graphical calculation based on the knowledge that the rate of reaction is independent of the gas velocity through the interstices

between the catalyst particles and is a function of temperature, pressure, and gas composition only.

When the reaction is carried out isothermally in a small volume of catalyst at two different space velocities, a higher per cent of ammonia is produced at the lower space velocity. This can be attributed to the longer residence time in the reactor at the lower space velocity. The rate of synthesis varies throughout the catalyst bed, owing to the increasing ammonia concentration. The difference between the ammonia formed at the low space velocity and that at the high, divided by the difference in residence time, is the rate of synthesis at the per

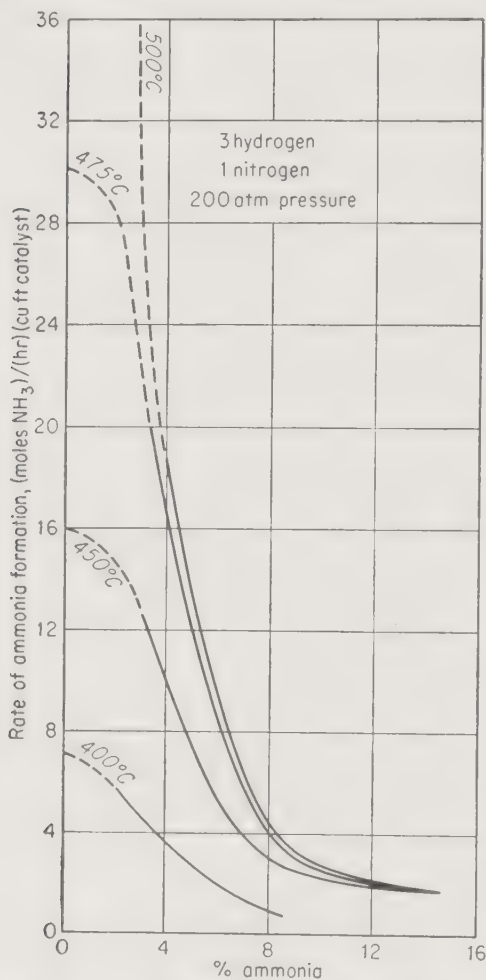


FIG. 12-15. Rate of ammonia formation at 200 atm. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**: 359 (1953).]

cent of ammonia represented by the average of the exit concentrations at the two space velocities. This calculation can be made exact and the need for averaging the gas compositions avoided by measuring the slope of the curve of conversion of nitrogen and hydrogen to ammonia (based on measured exit ammonia concentrations) vs. the reciprocal of the space velocity. In [Fig. 12-13] the experimental data shown in [Fig. 12-14] have been plotted as conversion to ammonia vs. the reciprocal of the space velocity. The slopes of these curves when divided by 359, the standard mole volume, give the rate of formation of ammonia as pound moles per hour per cubic foot of catalyst. The results are shown in [Fig. 12-15].

The rapid decrease in rate of reaction as the per cent ammonia increases is evident from these curves.

12-9. Temperature and Ammonia Concentration in the Reactor. The gas temperature, the gas pressure, the chemical equilibrium, the chemical reaction rate, the heat of reaction, and the transfer of heat and mass are interrelated, and these determine the behavior of the ammonia-synthesis reactor. Instead of attempting to

explain immediately the relationship between these factors in an actual reactor, this will be done in stages of increasing complexity. At first a simplified version of the reactor will be described, and later this idealized version will be modified so as to more closely resemble an actual reactor.

Isothermal Reactor. In this first version of a reactor, the pressure p and temperature T_r are to be considered constant throughout the catalyst bed. The gases leaving the catalyst bed flow countercurrent to the incoming gases in a heat exchanger. The temperature distribution in the heat exchanger and in the catalyst bed is shown in Fig. 12-16. In the heat exchanger, the product gases are cooled from T_r to the temperature T_{20} , and the incoming gases are heated from T_{1i} to T'_1 . The incoming gases then pass through tubes in the catalyst bed and absorb part of the heat of reaction. This raises their temperature from T'_1 to T_r . The operation as a whole is adiabatic, and the rise in temperature from T_{1i} to T_{20}

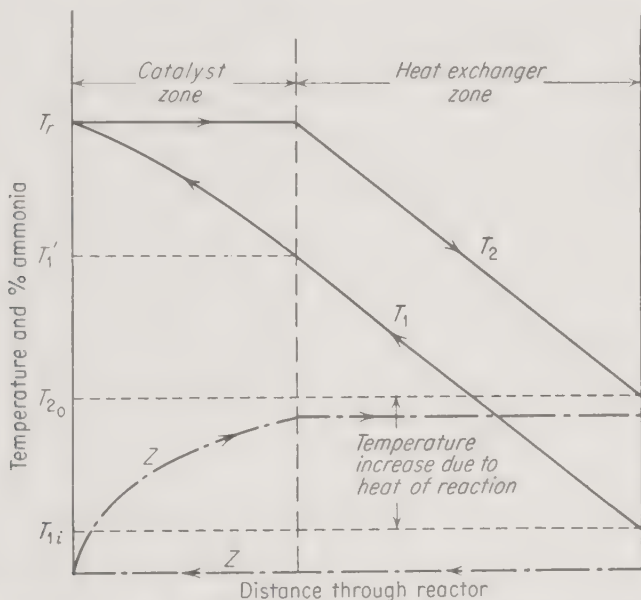


FIG. 12-16. Temperature and ammonia-concentration distribution in a simplified version of a reactor and heat exchanger.

accounts for the heat given off by the reaction. Under these conditions, the rate of synthesis of ammonia at any point in the catalyst would depend only on the per cent ammonia in the gas at that point, since it has been assumed that the temperature is constant. Thus, as ammonia is formed, the rate of synthesis will decrease, and the mole fraction of ammonia will increase approximately as shown in Fig. 12-16. It is evident that a constant reaction temperature cannot represent the true situation in a catalyst bed. This is evident since the highest rate of synthesis occurs at the inlet to the bed, and the temperature difference between the bed and incoming gases is least at this point. Hence, the temperature of the gas in the catalyst must rise near the gas inlet.

Adiabatic Reactor: Heat Exchanger in Catalyst Bed. A simplified but more realistic explanation of an ammonia-synthesis reactor has been given

by van Heerden.³⁵ Only the catalyst bed and the cooling tubes in it are considered. His explanation is as follows:³⁵

It is based on the most simple construction of a synthesis converter, consisting of a cylindrical catalyst vessel with a large number of countercurrent heat

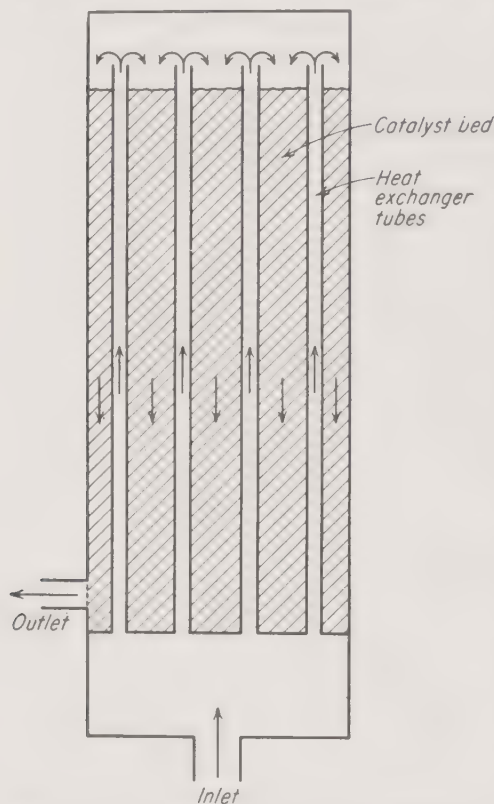


FIG. 12-17. Simple ammonia-synthesis converter. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

equals the heat of reaction produced in the column. This is approximately equivalent to the statement that the temperature difference between inlet and outlet gases is proportional to the fractional conversion.

The following assumptions are made:

1. There is no temperature difference between the catalyst granules and the interstitial gas.
2. The temperature in the catalyst bed is constant in any cross section of the converter.
3. As a consequence of the second assumption, the rate of heat exchange between the ascending and descending currents of gas is represented by an over-all heat transfer coefficient, U , which is constant throughout the converter.

³⁵ Reprinted from C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953). Copyright, 1953, by the American Chemical Society and reprinted by permission of the copyright owner.

exchanger tubes inside [see Fig. 12-17]. The cold nitrogen-hydrogen mixture enters the column at the bottom, flows upward through the heat exchanger tubes and downward through the catalyst bed, and leaves at the bottom. The degree of heat exchange can be varied by bypassing the upward flow in the heat exchanger tubes through a central tube of large diameter.

The characteristic temperature distribution in a converter of the type shown in [Fig. 12-17] is given in [Fig. 12-18]. Following the path of the gas stream, the temperature rises gradually inside the heat exchanger tubes. In the upper part of the catalyst bed where the heat of reaction exceeds the heat removed by the cooling tubes, the temperature rises and passes through a maximum value.

In the lower part of the converter the reaction rate decreases gradually, so that the bottom section mainly serves as a heat exchanger. The process as a whole is assumed to be adiabatic, which means that the heat content of the outlet gases above the inlet temperature

In the following calculations this rate of heat exchange will be expressed in terms of the height of transfer unit [HTU], $H = c/UA$, where c is the feed rate expressed as heat capacity per unit time and A is the total heat exchanging surface per unit of length of the converter.

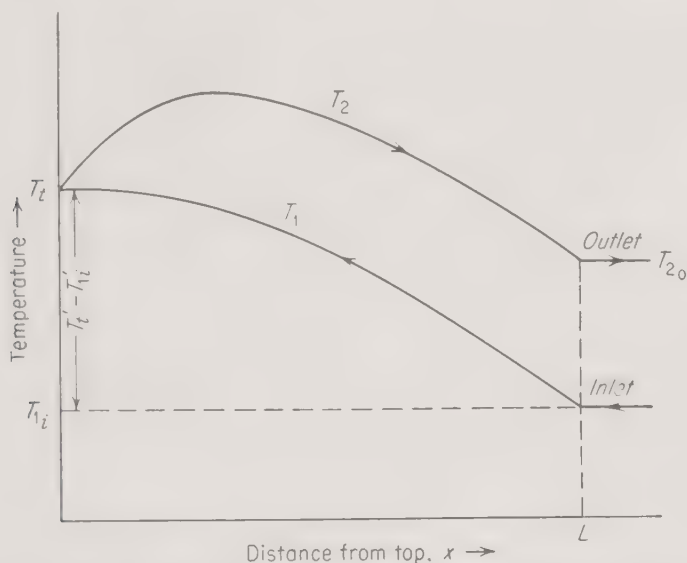


FIG. 12-18. Temperature distribution in synthesis converter with internal heat exchanger. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

4. The heat capacity of the gas is independent of temperature and conversion; the temperature rise, τ , of the reacting gas corresponding to the adiabatic formation of 1% of ammonia is constant and equals 15°C .

5. The reaction velocity satisfies the well-known relation of Temkin.^[32]

The original relation of Temkin reads:

$$\frac{dp_{\text{NH}_3}}{dt} = f_c \left(K'^{1/2} \frac{p_{\text{N}_2} p_{\text{H}_2}^{3/2}}{p_{\text{NH}_3}} - \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{3/2}} \right) \quad [(12-48)]$$

where K' is the equilibrium constant and f_c the temperature-dependent rate constant. After some modifications, substituting a nitrogen to hydrogen ratio of 1 to 3 and the temperature dependency of f_c , this relation can be written as:

$$\begin{aligned} \frac{dZ}{dx} &= F(Z, T) \\ &= \frac{2.4 \times 10^{12}}{V} p^{-3/2} (1+Z)(1-Z)^{1/2} e^{-20,000/T} \left[0.105 K'^{1/2} p^2 \frac{(1-Z)^2}{Z} - \frac{Z}{(1-Z)^2} \right] \end{aligned} \quad [(12-49)]$$

This relation was used in the numerical calculations where V is the linear gas velocity in the empty vessel and p is the total pressure.

6. No heat is lost to the surroundings.

7. The numerical data are as follows:

Height of converter, L , meters.....	12
Diameter of converter, meters.....	0.7
Pressure, atmospheres.....	300
N_2 to H_2 ratio.....	1 to 3
Inlet NH_3 , %.....	1.5
Inlet temperature, $^{\circ}C$	50
Linear gas velocity in empty vessel, meters per second....	0.16
Height of transfer unit (H), meters.....	3

The value of the height of the transfer unit, H , was estimated by a rough calculation, using literature data on heat transfer rates in packed columns. The value of 3 m must be considered as the minimum value obtained if the column is operated at its maximum heat exchanging capacity. By-passing of the heat exchanging tubes increases the value of the height of the transfer unit. The results of these calculations will prove that the values used are reasonable.

Starting from the above assumptions, the concentration and temperature distribution must satisfy the following differential equations:

$$-\frac{dT_1}{dx} = \frac{T_2 - T_1}{H} \quad [(12-50)]$$

$$\frac{dT_2}{dx} = \tau \frac{dZ}{dx} - \frac{T_2 - T_1}{H} \quad [(12-51)]$$

$$\frac{dx}{dZ} = F(Z, T_2) \quad [(12-52)]$$

$F(Z, T_2)$ is a modified formulation of the reaction velocity, obtained from the original rate equation of Temkin. After substitution of the given conditions, F was calculated as a function of T_2 for a number of Z values and plotted as a set of curves with Z as the parameter. The numerical values needed were found by interpolation.

For any value of Z there is some corresponding temperature, T_e , at which the gas mixture is in chemical equilibrium. This temperature is readily found by setting the term in brackets in Eq. (12-49) equal to zero. A value of K' is found for each value of Z and the temperatures corresponding to these K' values are T_e . Far below this equilibrium temperature the reaction rate increases rapidly with the temperature. Approaching T_e the function, F , passes through a maximum to become zero at T_e and negative above T_e .

The following tabulation, prepared for orientation purposes, gives values of the equilibrium temperature, T_e , the temperature of maximum reaction rate, T_m , the temperature, $T_{0.1}$ where the reaction rate is 0.1 times the maximum rate, and dZ/dx at T_m for some values of Z . In the last column the maximum reaction rate at T_m is given.

Because of the complexity of the function $F(Z, T_2)$ an analytical solution of the differential equations [(12-50) to (12-52)] is impossible. A numerical step-wise integration is the usual line of attack for this kind of problem.

Z	$T_e, ^\circ\text{C.}$	$T_m, ^\circ\text{C.}$	$T_{0.1}, ^\circ\text{C.}$	$dZ/dx_{\max.},$ mole fraction/m.
0.02	950	840	500	1.6
0.05	760	680	420	0.23
0.10	650	580	370	0.048
0.15	590	530	340	0.017
0.20	540	490	320	0.007

However, besides the differential equations [(12-50) to (12-52)] the solution must satisfy the following boundary conditions [see Fig. 12-18]:

$$T_2 = T_1 \quad \text{when } x = 0 \quad [(12-53)]$$

$$T_1 = T_{1i} \quad \text{when } x = L \quad [(12-54)]$$

Since one of the boundary conditions is at one end of the system and one at the other, a special stepwise calculation and graphical procedure were used to solve these equations and to obtain the distribution of temperature

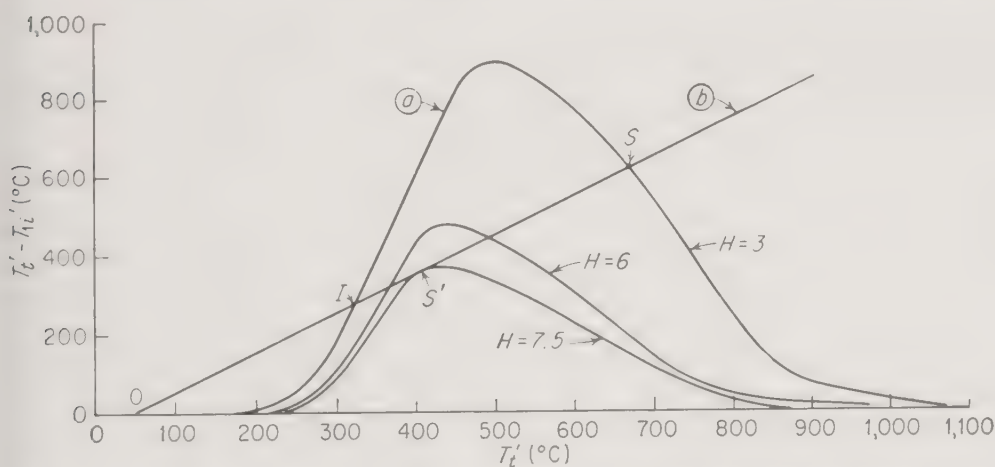


FIG. 12-19. Relation between assumed temperature T'_i and temperature rise of incoming gas $T'_t - T'_{1i}$. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

and ammonia concentration in the incoming and outgoing streams. An arbitrary temperature T'_i at $x = 0$, at the top of the catalyst bed, was chosen. A stepwise integration was carried out up to $x = L$. This resulted in values of T'_{1i} , T'_{2o} , and $Z'_{o'}$, but these are not the correct values as determined by the boundary condition (12-54). Other arbitrary values of T'_i were chosen, and the curve marked $H = 3$ m shown in Fig. 12-19 was prepared.

Because at low values of T'_i the reaction is slow, the temperature difference, $T_2 - T_1$, remains small, and according to [Eq. (12-50)] the total change in T'_1 ,

$T'_t - T'_{1i}$, during the integration will also be small. For $T'_t = T_e$, the equilibrium temperature for the inlet gas, the reaction rate is zero and T_2 and T_1 are constant throughout the integration. For a nitrogen to hydrogen ratio of 1 to 3 and an inlet percentage of 1.5% of ammonia, the equilibrium temperature equals 1080°C. Thus, in all calculated curves like that in [Fig. 12-19] $T'_t - T'_{1i}$ is zero for $T'_t = 1080^\circ\text{C}$. In the region between low temperature where the reaction rate is practically zero and the equilibrium temperature where the reaction rate becomes zero again, the $T'_t - T'_{1i}$, T'_t curves will show a maximum. For those points of the $T'_t - T'_{1i}$ curve which satisfy the condition $T'_t - T'_{1i} = T'_t - T_{1i}$ the corresponding solutions satisfy the boundary condition of [Eq. (12-54)].³⁵

This condition is represented by the straight line *b* in Fig. 12-19. This figure resembles Fig. 11-16 which was based on the analysis for a fixed and uniform reactor temperature. In the catalytic reactor under discussion, the temperature varies throughout the reactor. An analysis similar to that in Chap. 11 may be made in this case by choosing a suitable point in the reactor and relating the integrated behavior throughout the reactor to this point. This was the procedure which led to curve *a* in Fig. 12-19. The abscissa represents the assumed values of the temperature at the entrance to the catalyst bed, and the ordinate is the calculated rise in temperature of the gas from the inlet to the top of the catalyst bed. The curves *a* and *b* intersect at three points. The intersection at *O* represents the nonreacting state, at *I* the state of ignition, and at *S* the steady reaction state. The latter represents a solution to the differential equations which meets the boundary conditions.

If the ordinate of Fig. 12-19 is multiplied by the heat capacity of the feed, it represents a quantity of heat. Curve *a* is then the quantity of heat which must be transferred from the reaction space to the heat-exchanger tubes in order to satisfy the requirements imposed by Eqs. (12-50) to (12-52) for the rates of heat transfer and chemical reaction. Curve *b* is determined by the inlet and outlet conditions imposed on the heat-transfer tubes. The same method of analysis may be applied to reactors of different designs and for different methods of operation. Each case will require its own diagram, depending on the method used to carry out the integration of the differential equations. The diagram will always consist of an *a* curve, giving a heat quantity determined by the rate of reaction in the reactor space and the rate of heat transfer from the reactor space, and a *b* curve, giving a heat quantity determined by the boundary conditions, both as functions of a reference temperature.

In [Fig. 12-20] the complete temperature and concentration distribution is given corresponding to the steady state, *S*, in [Fig. 12-19]. Moreover, the variation of the equilibrium temperature throughout the converter is given. From this figure it is clear that the converter owes its stability to the fact that for an important part the reaction proceeds in the direct vicinity of chemical

equilibrium, where (between points P and Q) the reaction rate has a negative temperature coefficient.

The complete calculation was repeated for higher values of the H.T.U.—that is, for lower values of the heat exchanging capacity of the converter. The resulting a -curves for $H = 6$ and 7.5 meters are also given in [Fig. 12-19]. At $H = 7.5$ meters the limit of stability is reached and at still higher values auto-thermic reaction is no longer possible. The temperature and concentration distributions at $H = 7.5$ m are given in [Fig. 12-21], and from a comparison

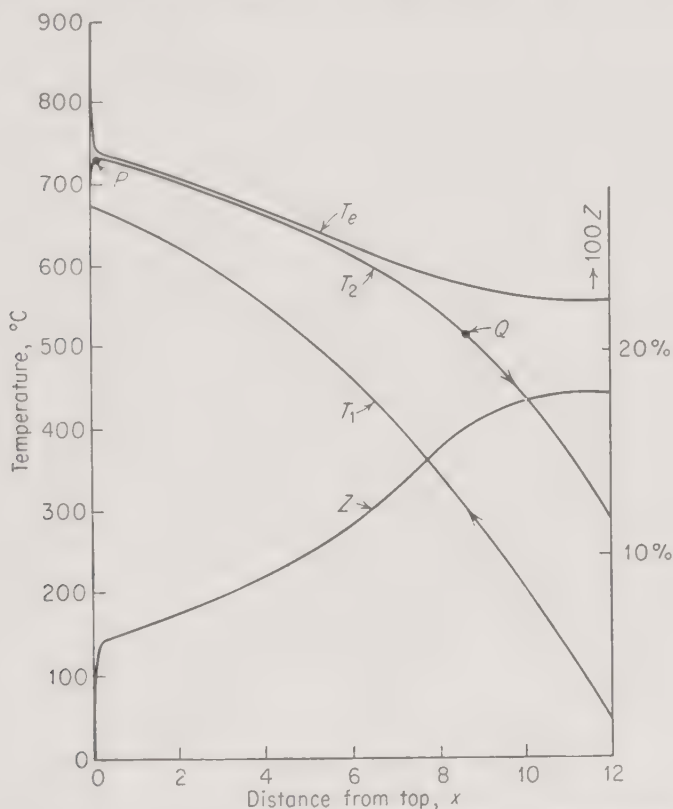


FIG. 12-20. Temperature and concentration distribution corresponding to stationary state S in Fig. 12-19. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

with [Fig. 12-20] it is clear that it is much better to operate the converter at the limit of stability. The temperature level is then much lower and the outlet ammonia concentration higher. The decrease in stability is demonstrated by the fact that the region PQ , where the reaction rate has a negative temperature coefficient, is much smaller in [Fig. 12-21] than in [Fig. 12-20].

These results are in complete agreement with practical experience. In practice, synthesis converters are always operated in such a way that some reference temperature—e.g., the temperature at the top of the column—is kept as low as possible, continuously taking care that the reaction does not cut out.

The influence of a decreasing activity of the catalyst is illustrated in [Fig. 12-22]. Here the a -curves are given for different values of the catalyst activity, accounted for in activity coefficient, f' , by which the reaction rate— $F(Z, T_2)$ in [Eq. (12-21)]—

is multiplied. The curves in [Fig. 12-22] correspond with $f' = 1, 0.5, 0.25$, and 0.15 and were calculated with $H = 3$ meters. At this value of H the limit of stability is reached for $f' = 0.15$ —that is, for a catalyst activity about seven times lower than the original value. Comparing the limit of stability at $f' = 1$ with that at $f' = 0.15$, it was found that the top temperature increases from 400 to 570°C , the H.T.U. value decreases from 7.5 meters to 3 meters, and the exit ammonia concentration decreases from 21.5 to 12% . These results are also

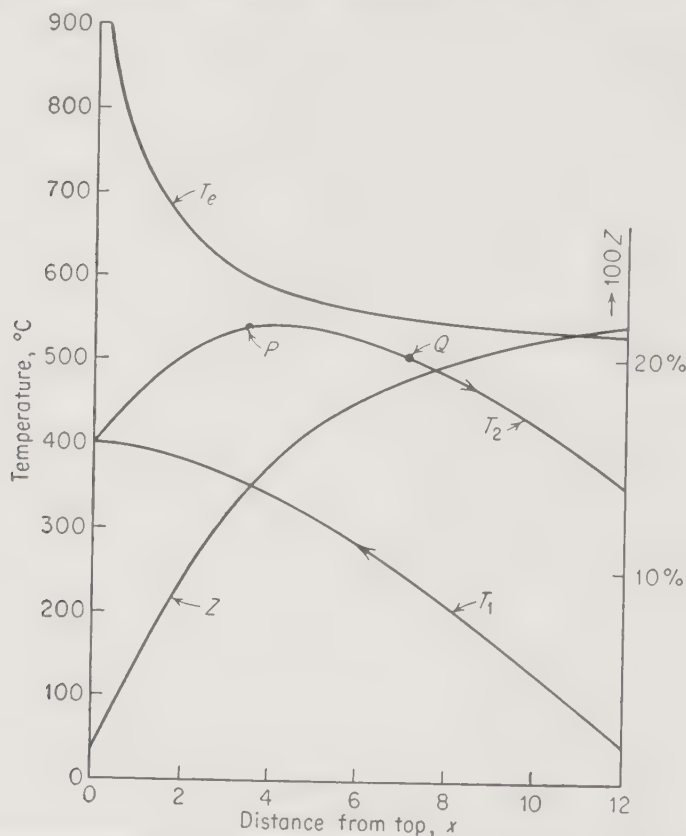


FIG. 12-21. Temperature and concentration distribution corresponding to stationary state S' at limit of stability in Fig. 12-19. [From C. van Heerden, *Ind. Eng. Chem.*, **45**: 1242 (1953).]

in agreement with practice, where because of the decreasing catalyst activity, the heat exchange capacity must be enlarged gradually. This is accompanied by a continual rise of the temperature level and a decrease in the degree of conversion.

Finally, the results obtained with different catalyst activities can be used as an orientation about the influence of a change in the feed rate. If it is assumed that the H.T.U. is independent of the gas velocity (because $H = c/UA$, $c \propto V$, and $U \propto V^{0.8}$, this assumption is approximately correct), it can be deduced from the differential equations [(12-50) to (12-52)] that an increase in feed rate is equivalent with a proportional decrease in catalyst activity. Thus the four curves of [Fig. 12-22] also apply by approximation to the conditions $f' = 1$ and $V = 0.16/f'$ meters per second. Again in agreement with practice, it follows

that an increase in the gas velocity necessitates an increase in the heat exchanging capacity and, consequently, operation at a higher temperature level.³⁵

Catalyst in Tube. Condition 2 under Adiabatic Reactor requires that the temperature be constant over any cross section of the catalyst. In reality a temperature variation usually exists across the catalyst bed. The methods developed in preceding sections may be applied to a reactor with the catalyst in a tube and the cooling gases around the tube to predict such a temperature variation. The heat is then transferred radially

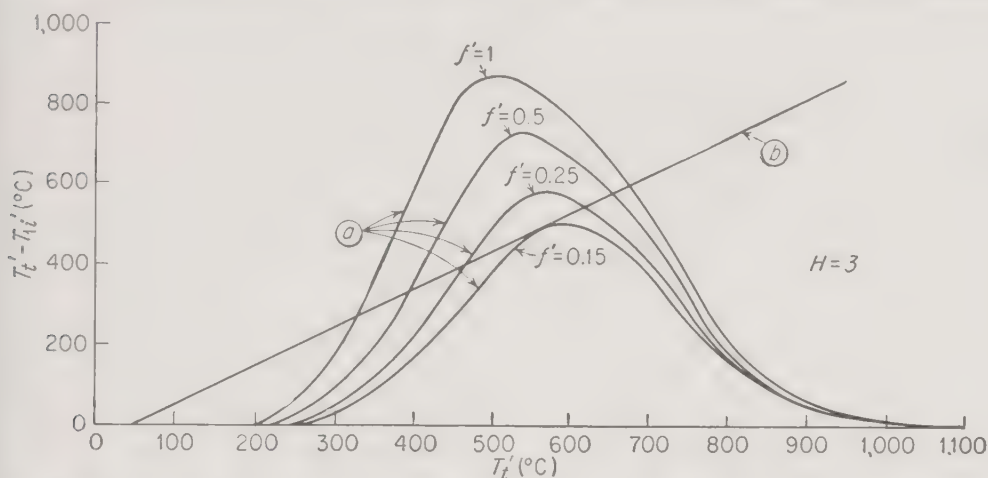


FIG. 12-22. Relation between assumed temperature T'_t and temperature rise of incoming gas $T'_t - T_1'$ for different values of catalyst activity. [From C. van Heerden, *Ind. Eng. Chem.*, **45**:1242 (1953).]

to the walls, and radial gradients of both temperature and per cent ammonia are found. A simple method using data such as represented by Fig. 12-15 and yielding the distribution of temperature and fractional conversion both radially and in the direction of flow is desirable. A method has been described in Chap. 11 and is developed further here.¹¹

The method proposed by Baron^[36] is a major step in this direction. The instantaneous rates $R_1\rho_B$ of ammonia formation from [Fig. 12-15] have been employed to calculate the relations required by Baron's graphical method for the following case. A 2-in. i.d. tube is packed with catalyst, and a gas mixture which is initially 3 to 1 hydrogen to nitrogen is passed through it at 200 atm. total pressure at a rate of 10,000 lb./ (hr.) (sq. ft.). The curves of $R_1\rho_B\lambda d_p \Delta z' / c_p G_0$ versus temperature at several values of per cent of conversion are shown in [Fig. 12-23]. The curves of $R_1\rho_B M_{av} d_p \Delta z' \times 10^2 / y_1^0 G_0$ vs. per cent of conversion at several values of temperature are shown in [Fig. 12-24]. Only preliminary graphical calculations were made for this one case, and these were not carried to the point where they provide a basis for firm conclusions. However, they indicated that near the inlet to the catalyst the reaction is fast enough so that radial temperature and concentration gradients are of less significance than the

³⁶ T. Baron, *Chem. Eng. Progr.*, **48**:118 (1952).

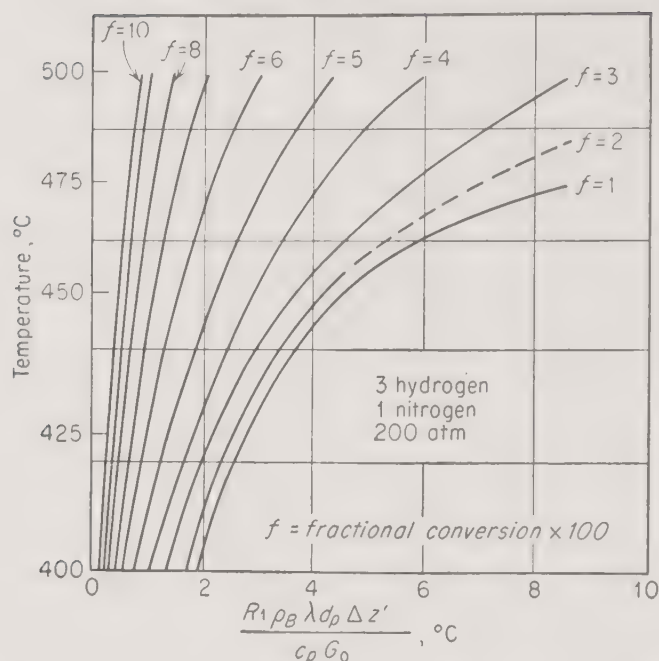


FIG. 12-23. Temperature increment curves for use in Baron's reactor-design method for conditions stated in text. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

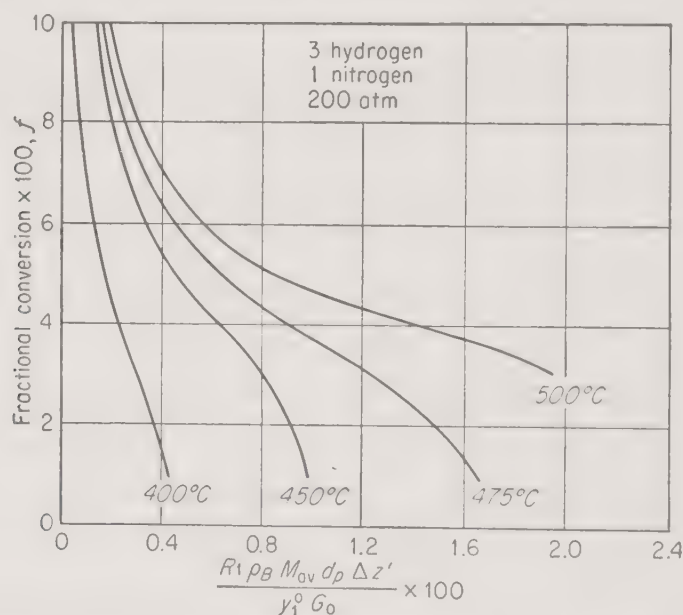


FIG. 12-24. Ammonia-conversion increment curves for use in Baron's reactor-design method. [From R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, **49**:359 (1953).]

axial gradients along the tube. The reaction in the catalyst proceeds at an increasing rate and is brought under control as a result of the depressing effect of the increasing concentration of ammonia on the reaction rate as well as by the cooling effect of radial heat transfer and to a lesser extent by the effect of approaching reaction equilibrium.

This is borne out by the axial temperature distribution in commercial reactors as shown in Fig. 12-25.

Industrial Reactor. The special case of the autothermal process provides a closely approximate interpretation of the synthesis of ammonia. The several assumptions listed will frequently need to be modified to interpret correctly the conditions observed in an actual catalytic reaction. A few of these modifications will be listed and discussed.

1. The relation of Temkin was developed for low pressures and requires modification to account for the deviations from the perfect-gas laws at pressures above 100 atm. Such modifications are described in Sec. 12-8.

2. Instead of a uniform temperature at any cross section, both temperature and concentration gradients are present. A method of allowing for these has been explained.

3. The activity of the catalyst is uniform throughout the bed when the catalyst is new, but poisoning is progressive starting from the inlet to the bed, and a constant activity coefficient f' cannot be applied to the whole bed after the catalyst has been in service for a time.

4. Heat is exchanged between the incoming gas and the gas in the catalyst bed, but it is also exchanged between the incoming gas and the gases which have left the catalyst bed as described for the isothermal reactor in this section.

The practical application of the theory and actual problems encountered in operating the ammonia converters at the Tennessee Valley Authority's plant are described by Slack, Allgood, and Maune³⁷ as follows:

The main objective in control of process variables in high-pressure ammonia synthesis, as in any other process, is to produce the required amount of product with a judicious balance between low operating cost, low risk of equipment damage and process interruption, and long life of equipment. An important function of the operating department is to determine the optimum balance between these factors. In ammonia synthesis the problem is complicated because of the fact that a general decline in process efficiency must be accepted as the catalyst loses activity. This necessitates changes in the balance between the various process variables during the life of the catalyst.

The variables involved are temperature, pressure, space velocity, ammonia content of gas entering the converter, content of inert constituents in the synthesis circuit, and hydrogen-nitrogen ratio.

Proper operating balance between variables is affected to a great extent, of course, by the amount of catalyst in the converter. From the operating standpoint, use of a generous amount of catalyst has a number of advantages. It allows a relatively wide variation in individual process variables, helping to offset any shortcomings which may exist or develop in other equipment in the synthesis circuit. Moreover, the large body of catalyst serves as a heat reservoir during temporary interruptions in production caused by trouble in other parts

³⁷ A. V. Slack, H. Y. Allgood, and H. E. Maune, *Chem. Eng. Progr.*, **49**:393 (1953).

of the plant. In many cases this makes it unnecessary to use the starting heater to get back to full operation, which is a slow and delicate operation.

The principal advantage of the large catalyst body, however, is the longer period of operation before recharging becomes necessary. In a plant of the T.V.A. type at least ten days are required to shut down and cool the converter, replace catalyst, and start up again. And after getting back on stream, a day or so usually elapses before the process can be fully tuned and brought back to full efficiency. Moreover, thermal stresses, accompanying the cooling and reheating, affect the life of the equipment and should be avoided, if possible.

In the T.V.A. plant the relatively large amount of catalyst installed has made it possible to operate until the converters needed shutting down anyway for internal repairs, thus making one shutdown cover both needs. Each of the converters contains about 144 cu. ft. (about 12 tons) of catalyst. This is roughly about twice as much catalyst as is used in some of the other 350 atm. processes.^[29] However, since the cost of the T.V.A. converters represented only about 3% of the total ammonia plant cost, the larger size of the converters was not a significant cost item, and the intangible value of long-term, uninterrupted operation is considered to be well worth the small additional cost involved.

The range of operating variables involved in maintaining production for more than eight years with the same catalyst is indicated in [Table 12-5]. Data given are typical ones from operation of train 1 and were selected from periods of approximately equal production rate. Also shown, to illustrate the shift in variables required to get higher production, are data taken near the beginning of the second catalyst run on train 1. At the beginning of this run production was increased to about 125 tons/(train)(day) as a result of the conversion to natural gas.

TABLE 12-5. TYPICAL CONVERTER OPERATING DATA†

Space velocity	Pressure, ‡ atm	Maximum temp., °F	Inerts in circulating gas, %	NH ₃ in gas to converter, %	NH ₃ in gas from converter, %	NH ₃ produced, tons/day	Comments
9,050	245	997	11.1	4.0	17.9	93	Near beginning of first catalyst run on train 1; train started 8/4/42
12,700	328	1051	7.9	4.0	13.8	91	Near end of first run; train shut down 2/5/51
13,200	263	991	11.1	5.3	18.1	122	Near beginning of second run on train 1

† From A. V. Slack, H. Y. Allgood, and H. E. Maune, *Chem. Eng. Progr.*, **49**:393 (1953).

‡ At converter outlet.

The most important single operating variable is the temperature in the catalyst bed. On this depends, to a great extent, both the life of the catalyst and the internal parts of the converter. Every effort is made to keep the temperature at as low a level as is practicable and also to prevent wide variations in temperature within the catalyst bed.

In the T.V.A. converters, catalyst temperature is measured by three thermocouples, the wells for which extend downward through the catalyst mass and are located in line on a diameter—one at the center and each of the other two about 10 in. from it. The thermocouples are adjustable vertically; the center one is normally kept at the point of maximum temperature, the control point for operation. The other two register inlet and outlet temperatures. In addition, the vertical temperature gradient is determined periodically.

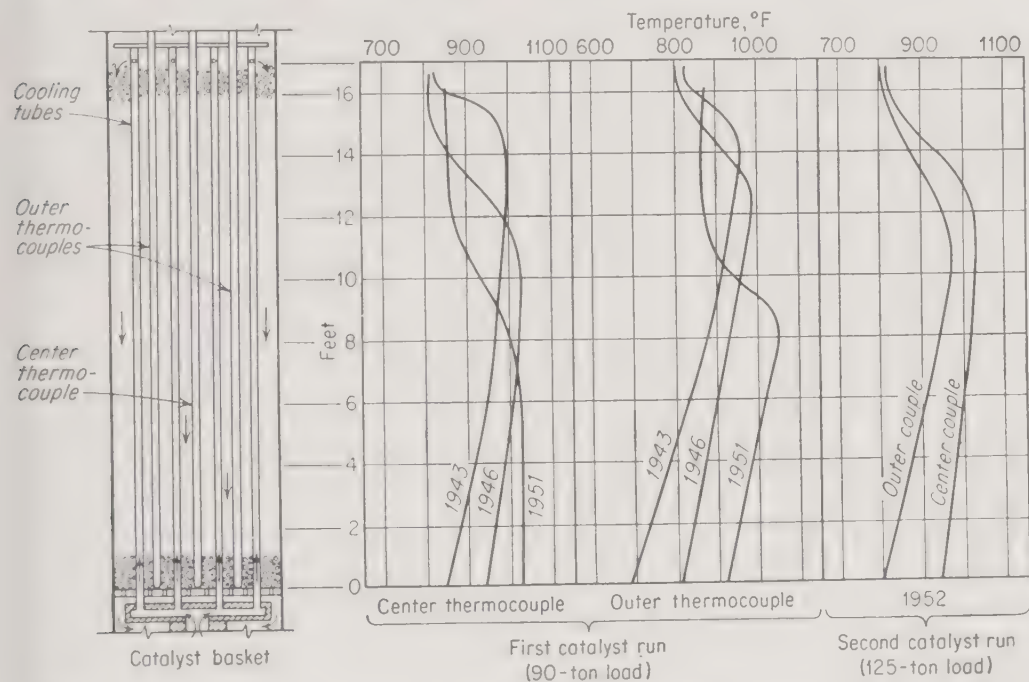


FIG. 12-25. Typical temperature distribution in catalyst. [From A. V. Slack, H. Y. Allgood, and H. E. Maune, *Chem. Eng. Progr.*, **49**:393 (1953).]

The range of temperatures encountered in the converter is illustrated in [Fig. 12-25]. One of the sets of data shown was taken in January, 1943, shortly after the beginning of the first catalyst run on train 1, the second in 1946, and the third in January, 1951, shortly before the end of the run. With the active catalyst in 1943, the curves are characterized by fast heat release as soon as the incoming gas strikes the catalyst. The maximum temperature is reached in about the first 2 ft. of travel through the catalyst; thereafter, transfer to the cooling tubes becomes faster than heat release from the continuing reaction, so that a drop of 200°F. or more occurs down through the remaining 14 ft. It would be better, of course, to have cooling tubes designed so that transfer of heat would be faster at the hot point than at other points, thereby evening out the catalyst temperatures. This appears impracticable, however, since the hot

point does not remain in the same place throughout a catalyst run. [Figure 12-25] shows that the point of maximum temperature had dropped 3 to 4 ft. by 1946 and was down in the lower half of the converter by the end of the run. In view of this, the best design appears to be a simple straight tube with a core tube to give maximum transfer rate.

Although the hot point was at about 1000°F. at the beginning of operation, the bulk of the catalyst was below 900°F. and a considerable portion below 800°F. It would have been possible to operate at an even lower temperature, since both space velocity and pressure were at relatively low levels [see Table 12-5] and these could have been increased to balance the adverse effect of lower temperature on space-time-yield. However, the rate of conversion drops off fast as the temperature is lowered below the 800–900°F. range, with the result that the reaction becomes difficult to control. At the higher temperature levels an accidental off-balance in a process variable such as a high hydrogen-nitrogen ratio ordinarily would affect operation only by causing the hot point to move downward a little in the converter. At lower temperatures, however, the same deviation might “blow out” the reaction with the result that catalyst temperature and production would fall off, and general re-tuning of the unit would be required. For this reason the temperature is kept high enough to cushion the effect of minor changes in process conditions. The higher temperature also allows lower space velocity and pressure, with a consequent economy in compression and circulation.

As the catalyst gets older, an increase in average temperature is required not only to give the temperature cushion, but also to aid in maintaining production after the other variables have been pushed to their limits. [Figure 12-25] shows that the increase in maximum temperature was held to about 50°F. over the 8½-year run, although the average temperature of the catalyst increased considerably more as is indicated by the increase of about 200°F. at the outlet.

The problem of temperature control in the converter is complicated by the necessity of keeping the converter shell cool. In high-pressure design it is desirable to keep parts subjected to high pressure stress at as low a temperature as possible and to keep parts subjected to high temperature as free of pressure stress as possible. As shown in [Fig. 11-9] the T.V.A. converter shell is insulated from the hot catalyst by a layer of insulation inside the catalyst basket and by a stream of cooling gas passing down between the basket wall and the shell. The shell was originally insulated on the outer surface to prevent excessive loss of heat which the cooling gas picks up in the preheater. However, when the plant was started up, it was found that the upper part of the shell (around the catalyst basket) could not be kept below 450°F., which was considered to be the upper limit from the standpoint of avoiding excess hydrogen attack on the shell. Two measures were taken: (1) the insulation was stripped off the upper section and a shield set around it so that a draft of air passed up between the shield and the shell, and (2) an additional line was installed to provide more cooling gas to the top of the converter. These steps have made it possible to keep the maximum shell temperature down to the present level of 150°–200°F.

One difficulty brought about by cooling the shell is a radial temperature differential in the catalyst. As shown in [Fig. 12-25] a differential of up to 150°F.

exists between the center and outer thermocouples, a distance of only about 10 in. Structural limitations prevent placing of thermocouples nearer the catalyst basket wall, but it can be assumed that a further drop occurs in the remaining 12 in. from the outer couple to the wall. It appears that better insulation of the catalyst basket or more cooling in the central zone of the catalyst is needed.

Also shown in [Fig. 12-25] is a temperature survey taken in February, 1952, after the train 1 converter had been in operation for about eight months with a new charge at the higher rate of about 125 tons/day. As might be expected, the hot point is lower in the catalyst bed and the general temperature level is somewhat higher than in 1943 near the beginning of the first catalyst run, during which the converter operated at a 90-ton rate.

Pressure and space velocity also require adjustment to offset loss of catalyst activity. As is shown in Table [12-5], both these factors were increased considerably during the 8½ year run. As has been noted, this train (No. 1) was shut down primarily because the plant was being converted to use of natural gas rather than for catalyst failure, although the catalyst clearly had lost much of its activity. Conceivably, the converter could have been operated for a longer period. Pressure could not have been increased much more, since it was close to the design limit of 350 atm., but space velocity could have been increased to about 25,000 at 350 atm., the design capacity of the circulators. The limiting factor probably would have been control of converter temperature at the higher velocity. At some point, either in velocity increase or in catalyst-activity loss, the hot point would get so low in the converter that any further increase would "blow out" the reaction. At that point the velocity (and therefore production) would have to be decreased to maintain control.

The remaining variables, hydrogen-nitrogen ratio and content of inert constituents and of recirculated ammonia in the circulating gas, present little in the way of operating problems. The recirculated ammonia is ordinarily kept as low as the refrigeration capacity will allow. Inerts are ordinarily not allowed to increase above the range of about 8 to 14% because of the adverse effect on ammonia content of gas leaving the converter, which is kept as high as possible because of limited refrigeration capacity. The hydrogen-nitrogen ratio is kept a little high on the nitrogen side to offset the higher loss of nitrogen dissolved in the product ammonia; it has been found that the nitrogen-hydrogen ratio in the gas flashed off from the ammonia weigh tanks is somewhat higher than in the make-up gas, which indicates a higher solubility for the nitrogen.

12-10. Recovery of Ammonia. The ammonia produced in the converter may be recovered from the mixture with the unreacted gases either as an anhydrous liquid or as an aqueous solution. The aqueous solution results from scrubbing the gases with water in a suitable tower. This method is especially suited for use on converted gas mixtures containing low ammonia concentrations in the range from 5 to 10 per cent. It introduces water vapor into the gases and this must be carefully removed, before the unreacted gases are recirculated to the converter, to prevent poisoning of the catalyst. The high solubility of ammonia in water makes

it possible to remove the ammonia almost completely from the residual nitrogen-hydrogen mixture. The purge gases are scrubbed with water before they leave the system.

Anhydrous liquid ammonia is obtained by condensing it from the mixture of $\text{NH}_3\text{-H}_2\text{-N}_2$ at sufficiently low temperatures. This method of ammonia recovery is used in the processes producing in excess of 10 per cent ammonia in the gases from the converters. The partial pressure of ammonia in the high-pressure gas must be greater than the vapor pressure of liquid ammonia to cause condensation at the temperature of the cold surface in the condenser. When the per cent ammonia in the gas and the total pressure are high, a sufficiently low temperature may be

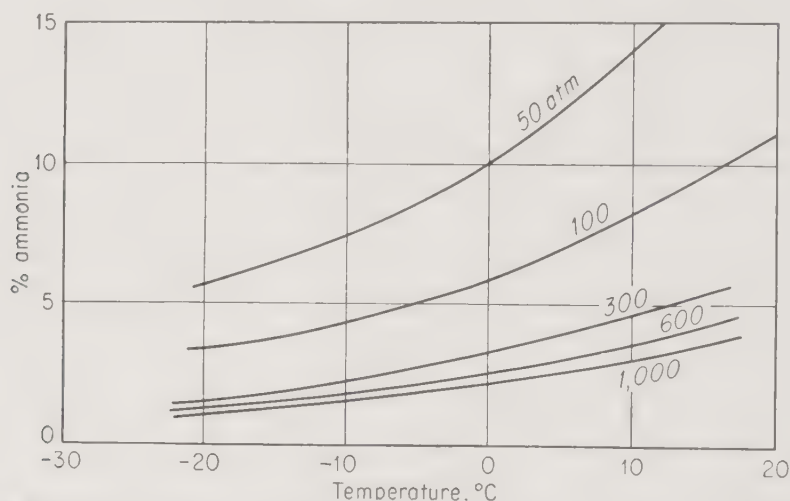


FIG. 12-26. Per cent ammonia in 3:1 hydrogen-nitrogen gas in phase equilibrium with liquid ammonia. [From A. T. Larson and C. A. Black, *J. ACS*, **47**:1015 (1925).]

obtained with cooling water alone. Under other conditions, with lower partial pressures of ammonia in the gas, a refrigeration system is required to reach a temperature low enough for recovery by condensation. The per cent ammonia in 3:1 hydrogen-nitrogen mixtures in equilibrium with liquid ammonia^{37a} is given in Fig. 12-26. The maximum per cent recovery of anhydrous liquid ammonia by condensation for several conditions is shown in Table 12-6.

The design of the anhydrous-ammonia separator is especially important. Under high pressure, the density of the synthesis-gas mixture and the liquid ammonia approach each other and make complete removal of the liquid difficult.

12-11. Removal of Inert and Excess Gases. The synthesis mixture used in commercial processes contains small percentages of inert gases such as argon and other rare gases, and methane. These gases do not

^{37a} A. T. Larson and C. A. Black, *J. ACS*, **47**:1015 (1925).

poison the catalyst, and the cost of removing them from the hydrogen-nitrogen mixture has not been considered justified in the past. If pure hydrogen-nitrogen mixture in precisely the stoichiometric ratio were used, the converter could be operated by adding make-up gas equivalent to the ammonia formed without discharging gas from the system. Inert gases together with small excesses of hydrogen or nitrogen resulting from small deviations from stoichiometric proportions, however, accumulate in the

TABLE 12-6. MAXIMUM PER CENT RECOVERY OF ANHYDROUS LIQUID AMMONIA BY CONDENSATION^{37a}

Pressure, atm	NH ₃ in gas from converter, %	Condenser temperature, °C	Ammonia recovered, %	Ammonia in gas from condenser, %
1,000	25	20	86	4.4
600	25	20	84	5.0
300	15	20	80	6.3
300	15	-5	91	2.8

system and must be removed. The removal of these gases is accomplished by purging a small percentage of the gas before the remainder is recycled. The concentration of inerts in the recirculated gas is allowed to reach a steady value several times that in the make-up gas. The rate of introduction of inert gas and excess reactant in the make-up gas is the same as the rate of their removal in a smaller volume of purged gas.

Example 12-1. A synthetic-ammonia plant is supplied with gas containing 74.8 per cent H₂, 24.6 per cent N₂, and 0.40 per cent CH₄ and other inerts. The gas from the converter contains 14 per cent ammonia, and 90 per cent of this is recovered as product and the rest recycled with the unconverted gases. The purged gas after complete removal of ammonia contains 9.0 per cent inerts. Calculate (a) the per cent conversion of the inlet gas to ammonia, (b) the ratio of recycle to fresh feed gas, and (c) the composition of the gas entering the converter.

Solution. (a) Basis: 100 moles purge gas

$$\text{Moles inerts} = 9.0$$

$$\text{Moles excess H}_2 \text{ in purged gas} = (74.8 - 24.6 \times 3) \frac{9.0}{0.4} = 22.5$$

$$\text{Moles N}_2 \text{ in purged gas} = (100 - 9.0 - 22.5) \frac{1}{4} = 17.1$$

$$\text{Moles N}_2 \text{ in feed gas} = 9.0 \times \frac{0.246}{0.004} = 554$$

$$\text{Per cent conversion} = \frac{554 - 17.1}{554} = 97.0$$

(b) Basis: 100 moles make-up feed gas

$$\text{Moles NH}_3 \text{ in product} = 24.6 \times 0.97 \times 2 = 47.7$$

$$\text{Total moles from NH}_3 \text{ separator} = \frac{47.7(1 - 0.14 \times 0.90)}{0.14 \times 0.90} = 331$$

$$\text{Per cent NH}_3 \text{ in recycle gas} = \frac{14.0 \times 0.1}{1.00 - 0.14 \times 0.90} = 1.6$$

$$\text{Moles purge gas} = \frac{0.4}{0.090 \times (1 - 0.016)} = 4.52$$

$$\text{Moles recycle gas} = 331 - 4.5 = 326.5$$

(c)

$$\text{Per cent inerts in recycle gas} = \frac{0.4 \times 100}{4.52} = 8.85$$

NH₃ and inerts in gas entering the converter,

$$\text{Mole per cent NH}_3 = \frac{1.6 \times 325}{425} = 1.2$$

$$\text{Mole per cent inerts} = \frac{0.0885 \times 325 + 0.4}{425} = 6.9$$

N₂ and H₂ in gas entering the converter,

$$\text{Mole per cent excess H}_2 = 6.9 \times \frac{22.5}{9.0} = 17.2$$

Mole per cent of 3:1 H₂-N₂ mixture

$$= 100 - 17.2 - 6.9 - 1.2 = 74.7$$

$$\text{Mole per cent N}_2 = \frac{74.7}{4} = 18.7$$

$$\text{Mole per cent H}_2 = 74.7 \times \frac{3}{4} + 17.2 = \frac{73.2}{100.0}$$

For a higher conversion or when the inerts are a greater percentage of the make-up gas, the purge from the first recirculation system may be fed to a second converter system and the unreacted gases from this recycled to the second converters. The per cent inerts in this second recirculation system is then higher than in the first. The advantage of this system is that the higher percentage of inerts is present in only a fraction of the ammonia-converter capacity. This method may be repeated with the purge gases from the second converter system being fed to a third. In this way, the inert-gas content in the final recirculating system may be 20 to 30 per cent.

A series of single-pass converters has been used in those processes where a high per cent conversion is obtained in the converter, such as in the Claude process. In the Claude process the gas leaving the first converter contains over 25 per cent ammonia, representing a 45 per cent conversion of the entering nitrogen-hydrogen mixture. In the plant at Yazoo City,

Mississippi,²³ the purge gas (on an ammonia-free basis) normally analyzes about 20 per cent methane, 19 per cent nitrogen, 58 per cent hydrogen, and 3 per cent argon, and this results in an over-all conversion of 90 per cent of the original hydrogen and nitrogen.

The lower-pressure plant at Vicksburg²⁰ removes the methane and argon in the nitrogen wash system, and the need for purging the synthesis loop is substantially reduced.

12-12. Economics of Process Selection. The ammonia-synthesis converter is the heart of the process, but preparation and purification of the nitrogen-hydrogen mixture account for the greater part of the cost of producing ammonia. A number of variations in the synthesis step and in the gas-preparation steps are possible. The selection of a process from among the possible choices is based on an economic evaluation. Comparisons of costs have been published for several cases, such as for natural gas vs. coal as a source of synthesis gas;³⁸ for the 1,000-atm Claude process vs. a conventional 200 to 350 atm process;²³ for four modifications of a 120-ton/day plant for operation at 350 atm using natural gas as a source of synthesis gas;³⁹ for five different raw materials;⁴⁰ and for the pressure reforming of natural gas.⁴¹

Economic Evaluation of Four Processes. The following quotations³⁹ will serve as an illustration of an economic analysis.

Four cases were set up for evaluation, a base case with conventional primary and secondary reforming and three with the proposed improvements: Case I, the conventional process; Case II, primary and secondary reforming at an elevated pressure; Case III, air partial oxidation at a low pressure; and Case IV, air partial oxidation at an elevated pressure. The essential differences are shown in [Table 12-7].

Process designs were prepared for these four cases in order to obtain equipment lists for cost estimating purposes and utility requirements.

In all cases, the final purification step is methanation. In cases III and IV, this is preceded by a nitrogen-condensation step. The gas from the partial oxidation of natural gas with air contains an excess of nitrogen, and this excess is removed by condensation at low temperatures and elevated pressure. Methane and argon are removed with the liquid nitrogen.

The estimates do not need to be of a high degree of accuracy since only comparisons are desired. Care must be taken, however, to insure that costs of major items of equipment are determined on a comparable basis. Piping and structural steel are taken as 25 and 3 per cent, respectively, of the major equip-

²³ L. C. Skinner, H. R. Batchelder, Sidney Katell, *Ind. Eng. Chem.*, **44**:2381 (1952).

³⁹ B. J. Mayland, E. A. Comley, and J. C. Reynolds, *Chem. Eng. Progr.*, **50**:177 (1954).

⁴⁰ B. S. Duff, *Chem. Eng. Progr.*, **51**(1):12J (1955).

⁴¹ A. G. Eickmeyer and W. H. Marshall, Jr., *Chem. Eng. Progr.*, **51**(9):418 (1955).

ment. Other construction items, such as electrical, insulation, painting, etc., as well as freight, are set at the same value in all cases. A 5 per cent contingency is then added with allowance for items which already contain the manufacturer's contingency. The cost of erection is taken as 35 per cent of the total with allow-

TABLE 12-7. SUMMARY OF FLOW SCHEMES EMPLOYED TO PREPARE AND PURIFY AMMONIA-SYNTHESIS GAS†

Case	Primary and secondary reforming		Air partial oxidation	
	Conventional	Elevated pressure	Low pressure	Elevated pressure
	I	II	III	IV
Inlet pressure, psig....	45	150	45	350
Preparation step.....	Primary and secondary reforming	Primary and secondary reforming	Air partial oxidation	Air partial oxidation
Purification step (a)...	CO conversion	CO conversion	CO conversion	CO conversion
Purification step (b)...	CO ₂ absorption	CO ₂ absorption	CO ₂ absorption	CO ₂ absorption
Purification step (c)...	CO conversion	CO conversion	Compression to 266 psig	Condensation
Purification step (d)...	CO ₂ absorption	CO ₂ absorption	Condensation	Methanation
Purification step (e)....	Methanation	Methanation	Methanation	
Compressor suction, psig.....	9	105	234	234
Inerts in synthesis gas, %.....	1.30	1.30	0.34	0.34
SCF of synthesis gas per ton NH ₃	99,750	99,750	91,600	91,600
Conversion of useful gas, %.....	90.4	90.4	97.5	97.5

† From B. J. Mayland, E. A. Comley, and J. C. Reynolds, *Chem. Eng. Progr.*, **50**:177 (1954).

ance for items which already include the erection cost. Estimates of the other sections of the plant are based upon previous studies and are evaluated on a dollar per unit of capacity basis. Other costs such as fees, engineering, purchasing, and field charges are included as plant investment items.

The manufacturing cost per ton of ammonia is used for the final comparison of the processes. The plant investment affects directly the cost of producing ammonia. Fixed costs and maintenance are expressed as a percentage of the total plant investment. Other costs included are those for natural gas, cooling water, electric power, steam as equivalent natural gas, catalyst, chemicals, oper-

ating labor and overhead, supervision and control, and operating supplies. The cost per ton of ammonia depends upon the plant location. The cost schedule is based upon a south-central location. The cost per ton of ammonia is shown in [Table 12-8].

TABLE 12-8. OPERATING COST 120-TONS/DAY ANHYDROUS-AMMONIA PRODUCTION†

Case	Cost per ton			
	I	II	III	IV
Natural gas at 22¢/MSCF				
(a) Process.....	\$ 4.91	\$ 4.91	\$ 5.46	\$ 5.85
(b) Process fuel (including purge credit)....	2.02	2.53	0.55	0.68
(c) Steam generation.....	2.95	2.55	3.63	1.08
Cooling water at 1.5¢/1,000 gal.....	1.19	1.15	1.19	0.83
Electric power at 0.6¢/kwhr.....	5.16	4.06	6.31	5.32
Catalyst.....	1.60	1.57	0.94	0.94
Chemicals.....	0.24	0.24	0.82	0.82
Operating labor and overhead at \$2.25/hr (6 operators per shift).....	2.70	2.70	2.70	2.70
Supervision and control at 50% of operating labor.....	1.35	1.35	1.35	1.35
Plant maintenance at 3% of investment per yr.....	2.90	3.00	2.84	2.50
Operating supplies.....	0.65	0.65	0.65	0.65
Fixed costs at 12.5% of investment per yr.....	12.10	12.54	11.83	10.43
Total.....	37.77	37.25	38.27	33.15

† From B. J. Mayland, E. A. Comley, and J. C. Reynolds, *Chem. Eng. Progr.*, **50**:177 (1954).

Operation of the conventional primary and secondary reformer at elevated pressures, as shown by Cases I and II, results in improvement but not large for the particular price structure chosen. Because of the greater number of smaller tubes with thicker walls, the investment in the primary furnace is increased appreciably. A saving in compressor investment offsets only part of this. The resulting higher fixed costs are more than offset, however, by a saving in compression cost. More fuel is used in pressure operation because of the higher temperature level required to reduce the residual methane. Most of this extra heat, but not all, is recovered and is reflected as lower steam cost.

Air partial oxidation at essentially atmospheric pressure, Case III, shows only a slight improvement over conventional reforming investment. There is considerable saving in natural gas but a compensatory increase in the power requirement. The higher power requirement is due to compression of the excess nitrogen to 250 psig for removal by the low temperature separation. The result is a somewhat higher cost for the production of ammonia.

Air partial oxidation at elevated pressure has an advantage over the conventional process. As shown in the tabulation for Case IV, a substantial saving in the total production cost is made. Further, the required investment is down

about 12 per cent. The saving in natural gas is realized exclusive of steam generation. By the condensation of process steam from the carbon monoxide shift in the Girbotol stripper, a considerable saving in steam generation is effected. The saving in compression for the reformed gas by operation at an elevated pressure is more than offset by the required compression power for the air resulting

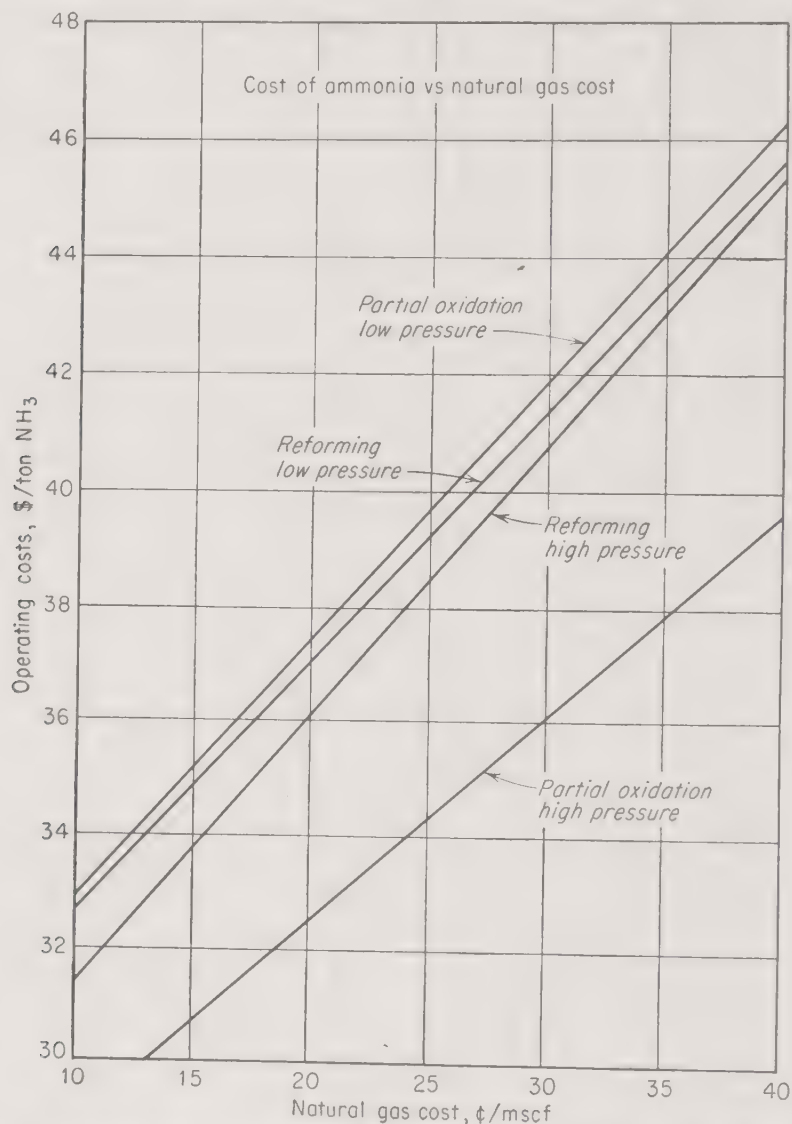


FIG. 12-27. Comparative cost of ammonia processes vs. cost of natural gas. (From B. J. Mayland, E. A. Comley, and J. C. Reynolds, *Chem. Eng. Progr.*, **50**:177 (1954).)

in a net increase. Other savings in cooling water, catalyst, and plant maintenance contribute a small amount of the total.

The results obtained in an analysis such as this are dependent to some extent on the price structure used. It is interesting to show the effect of higher natural gas prices on the cost of production. In [Fig. 12-27] is plotted total cost of production per ton of anhydrous ammonia vs. cost of natural gas. The advantage for Case IV is considerably greater at the higher natural gas price, whereas

pressure operation of a conventional reformer becomes increasingly attractive at the lower natural gas costs.

An economic comparison as presented in this paper is useful in establishing relative merits of various process schemes. However, care should be exercised in drawing conclusions from this type of study. According to the foregoing analysis, air partial oxidation under pressure has been shown to be economically advantageous, whereas atmospheric pressure operation is not particularly interesting. However, either atmospheric or pressure operation has other potential advantages which have not been credited. These are adaptability of the process to other fuels such as liquid hydrocarbons and use of the process in conjunction with an already existing hydrogen stream. In any particular study these factors may be very important and influence the choice of process. Disadvantages not considered in this study, are, of course, the unforeseen difficulties which might be encountered in engineering and constructing the plant for carrying out this process. With the conventional process, plant experience has shown what to expect in the way of maintenance, catalyst life, and fuel economy.

Pilot plant tests on the air partial oxidation step have been undertaken. The data so far obtained, as well as commercial plant data at moderate pressures, have demonstrated the operating feasibility of the process under the conditions used.³⁹

NOMENCLATURE

- A* Heat-exchanging surface per unit length of catalyst bed
b Constant
C_p Heat capacity of gases, cal/(g mole)(°K)
c_p Heat capacity of gases, Pcu/(lb)(°C)
c Feed rate of gas expressed as heat capacity per unit time
d_p Equivalent diameter of catalyst particles, ft
 ΔF° Standard free-energy change for a chemical reaction
f Fugacity; \bar{f}_{H_2} fugacity of hydrogen in a mixture, etc., atm
 \bar{f}' Catalyst activity coefficient, dimensionless
 \bar{f} Fractional conversion of limiting reactant
g A constant
G₀ Superficial mass velocity, lb/(hr)(sq ft)
H Height of transfer unit (HTU), c/UA , m
 ΔH Molal enthalpy change of the reaction; ΔH° , standard molal enthalpy change
h Constant
K Chemical equilibrium constant for the reaction
 $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3$
K' Chemical equilibrium constant for the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 K_ϕ^* Ratio of fugacity coefficients $\frac{\bar{\phi}_{\text{NH}_3}}{\bar{\phi}_{\text{H}_2}^{1/2} \bar{\phi}_{\text{N}_2}^{1/2}}$
K_p Chemical equilibrium constant based on partial pressures and Eq. (12-1)
k, k', k_c Reaction-rate constants

k_a, k_d, k_1, k_2	Reaction-rate constants
L	Depth of catalyst bed
M_{av}	Average molecular weight of unreacted gas mixture
N	Moles of gas; N_{NH_3} moles of ammonia
N_0	Moles of hydrogen-nitrogen equivalent to the mixture of hydrogen-nitrogen-ammonia in the volume of catalyst W
n_A	Mole fraction of component A
p	Total pressure, atm
p_{N_2}	Nitrogen-gas pressure or partial pressure; p_{H_2} hydrogen partial pressure, etc.
P_{N_2}	Partial pressure of nitrogen in equilibrium with adsorbed nitrogen
R	Gas-law constant
R_1	Rate of ammonia formation, moles NH_3 /(hr)(lb of catalyst)
R_a	Rate of nitrogen adsorption, moles/(hr)(lb of catalyst)
R_d	Rate of nitrogen desorption, moles/(hr)(lb of catalyst)
s	A constant
T	Temperature, °K
T_r	Temperature in isothermal reactor, °C
T_1	Temperature of gas before reaching the catalyst; T_{1i} at inlet, T'_1 at exit from heat exchanger, T'_{1i} calculated for assumed T'_i
T_2	Temperature of gas in catalyst bed and in heat exchanger after leaving the catalyst bed; T_{2o} at outlet from heat exchanger, T'_{2o} calculated for assumed T'_i
T_t	Temperature at top of catalyst bed
T'_t	Assumed value of temperature at top of catalyst bed
T_c	Temperature of chemical equilibrium corresponding to mole fraction Z and pressure p
T_m	Temperature of maximum reaction rate corresponding to mole fraction Z and pressure p
t	Time
U	Over-all heat-transfer coefficient
U_0	Volume of nitrogen-hydrogen mixture (at standard conditions) entering the catalyst bed per unit time
v	Volume of 1 mole of gas
V_0	Space velocity U_0/W based on equivalent unreacted hydrogen-nitrogen mixture, hr^{-1}
V	Linear gas velocity in empty catalyst vessel, m/sec
W	Volume of catalyst, cu ft
x	Distance from top of catalyst bed
y	Mole fraction in the gas; $y_{N_2}^*$, mole fraction of nitrogen in gas in adsorption equilibrium with adsorbed nitrogen
y_1^0	Mole fraction of limiting component in unreacted gas
Z	Mole fraction of ammonia in gas
z	Compressibility factor pv/RT ; z_s at standard temperature and pressure; also distance in axial direction
z'	z/d
α	g/s

- β h/s
- θ Fraction of available reaction sites on a catalyst surface which are covered
- λ Heat of formation of NH_3 , Pcu/lb mole
- ρ Density, lb/cu ft
- ρ_c Pounds of catalyst per cubic foot
- τ Temperature rise of the reacting gas corresponding to the adiabatic formation of 1 per cent ammonia
- φ Volume fraction of voids in catalyst
- $\bar{\phi}_j$ Fugacity coefficient for component j in a mixture [see Eqs. (8-124) and (8-125)]
- $\bar{\phi}_{\text{N}_2}^*$ Fugacity coefficient of nitrogen in adsorption equilibrium with activatedly adsorbed nitrogen

APPENDIX A

UNITS AND DIMENSIONS

A number of different consistent systems of units are in use. For example, there are three common systems of English units, in each of which length is expressed in feet and time in seconds.¹ In the absolute system, force is expressed in poundals and mass in pounds. In the gravitational system, force is in pounds and mass in slugs. In the engineering system, which is widely used in chemical engineering, force is expressed in force pounds and mass in mass pounds. Some writers develop quantitative relations which are correct only for one or two of these systems, without showing what modifications would be made to permit the use of any of the three systems. It is highly desirable that writers develop general relations which give correct results in all systems. If this is not done, the system used should be clearly defined. The reader also must have an understanding of the nature of units and dimensions if he desires to convert measurements from one system of units to another. The purpose of this section is to clarify these matters without advocating the exclusive use of any one system.

Concept of Dimensions and Units. Quantities of different kinds are measured and relationships between these measurements are developed by scientists and engineers.

The number of kinds of quantities which might be measured is very large. Some of the more common kinds used in mechanics are listed in [Table A-1, column 1.] An amount of any quantity is measured by comparison with a unit amount of this same quantity. The amount measured is indicated as equivalent to so many units. Fortunately it is not necessary to provide primary units for each quantity since some of these may be obtained in terms of primary-unit amounts of some of the other quantities. Thus a volume may be measured by comparing it with a unit of its own kind (the gallon) or with a combination of units of another kind (the foot). In the first case the volume is expressed in gallons, and in the latter in cubic feet.

To describe the various quantities appearing in a given list, a minimum number of them may be selected as primary units, since the remaining (secondary) quantities may be defined in terms of these primary units. In order to obtain the minimum number of primary quantities, one must select those which cannot be measured in terms of one another and are therefore independent. More than the minimum number may be selected as primary units, but then those in excess of the minimum number can be measured in terms of the minimum number and are therefore not independent units. The kinds of quantities for which primary units are chosen, whether minimum or not, are the "dimensions," while the actual amounts of these quantities chosen as a unit are the "primary units." If length is chosen as one of the primary quantities,

¹ E. W. Comings, *Ind. Eng. Chem.*, **32**:984 (1940).

then length is a dimension and is here denoted by symbol L . Volume then becomes a secondary unit, involving L^3 . In consistent systems of units, which are the only kind discussed in this paper, the unit of volume equals the cube of the unit of length.

Considerable latitude is possible in the choice of the primary quantities or dimensions. Thus if area, A , were chosen as a primary quantity, the dimensions of volume could be $A^{3/2}$ and of length, $A^{1/2}$. This is usually not convenient.

Only the kinds of quantities used in mechanics will be considered. However, the applications of these principles to other fields should be evident. Experience has shown that the minimum number of dimensions suitable for making measurements in mechanics is three. Length, L , and time, θ , are commonly chosen as two of the three, and either mass, M , or force, F , as the third. All four are often chosen as primary, and then either of the last two may be expressed in terms of the other three.

The fundamental law of motion giving the relation between the quantities force, mass, and acceleration is

$$\text{Force} = \frac{1}{\beta} \times \text{mass} \times \text{acceleration} \quad (\text{A-1})$$

where $1/\beta$ is a proportionality constant. With length and time as two of the dimensions, three possible choices for the others will be considered. In each, acceleration has the dimensions $L\theta^{-2}$.

The absolute or dynamical dimension system selects mass as the third dimension. A quantity of force is measured as the product of a number of units of mass and a number of secondary units of acceleration. Thus in this system of dimensions, by definition, force = mass \times acceleration and force has the dimensions $ML\theta^{-2}$. [Equation (A-1)] indicates that

$$[ML\theta^{-2}] = \frac{1}{\beta} [M][L\theta^{-2}] \quad (\text{A-2})$$

and therefore β is unity and has no dimensions.

The gravitational or technical dimension system selects force as the third dimension and measures a quantity of mass as a number of units of force divided by a number of units of acceleration. Then by definition, mass = force/acceleration, and the dimensions of mass are $FL^{-1}\theta^2$. [Equation (A-1)] gives

$$[F] = \frac{1}{\beta} [FL^{-1}\theta^2][L\theta^{-2}] \quad (\text{A-3})$$

and again β is unity and has no dimensions.

A four-dimension system uses force, mass, length, and time as primary.² This system has been used for a number of years in many fields, such as engineering thermodynamics and chemical engineering. It will be referred to as the $FML\theta$ dimension system. Here a quantity of mass is measured in primary units of mass and a quantity of force in primary units of force. The latter unit is not equal to the product of unit mass and unit acceleration but is defined independently. [Equation (A-1)] now gives

$$[F] = \frac{1}{\beta} [M][L\theta^{-2}] \quad (\text{A-4})$$

and β has the dimensions $ML\theta^{-2}F^{-1}$ and a numerical value determined by the relative sizes of the four primary units. [In English units in the $FML\theta$ dimension system β is g_c (lb mass)(ft)/(lb force)(sec²).]

² P. W. Bridgman, "Dimensional Analysis," 2d ed., pp. 52, 54, Yale University Press, New Haven, Conn., 1931.

[Table A-1] gives a list of quantities and their dimensions in the three systems discussed. The dimensions in [column 4] for the $FML\theta$ system are so chosen that force has the dimension F and mass M , except in the case of viscosity which is given in terms of both $FL\theta$ and $ML\theta$, distinguished by the symbols μ and μ' , respectively. (The decision as to whether a given kind of quantity involves force or mass in its original concept is not always possible. Thus viscosity may be defined as force per unit area

TABLE A-1. QUANTITIES AND THEIR DIMENSIONS IN THREE SYSTEMS†

Primary dimensions	M, L, θ	F, L, θ	F, M, L, θ
Name of system	Absolute or dynamical or physical	Gravitational or technical	None or $FML\theta$
Length, L	L	L	L
Time.....	θ	θ	θ
Mass.....	M	$F\theta^2L^{-1}$	M
Force.....	$ML\theta^{-2}$	F	F
β , a constant.....	None	None	$ML\theta^{-2}F^{-1}$
Acceleration, a	$L\theta^{-2}$	$L\theta^{-2}$	$L\theta^{-2}$
Energy, work.....	$ML^2\theta^{-2}$	FL	FL
Energy/unit mass.....	$L^2\theta^{-2}$	$L^2\theta^{-2}$	FLM^{-1}
Force/unit mass, a/β	$L\theta^{-2}$	$L\theta^{-2}$	FM^{-1}
Local acceleration of gravity, g_L	$L\theta^{-2}$	$L\theta^{-2}$	$L\theta^{-2}$
Diameter, D	L	L	L
Pressure, p	$ML^{-1}\theta^{-2}$	FL^{-2}	FL^{-2}
Power.....	$ML^2\theta^{-3}$	$FL\theta^{-1}$	$FL\theta^{-1}$
Mass velocity, G	$M\theta^{-1}L^{-2}$	$F\theta L^{-3}$	$M\theta^{-1}L^{-2}$
Linear velocity, V	$L\theta^{-1}$	$L\theta^{-1}$	$L\theta^{-1}$
Momentum.....	$ML\theta^{-1}$	$F\theta$	$ML\theta^{-1}$
Absolute viscosity, μ	$F\theta L^{-2}$	$F\theta L^{-2}$
Absolute viscosity, $\mu' = \mu\beta$	$ML^{-1}\theta^{-1}$	$ML^{-1}\theta^{-1}$
Density, ρ	ML^{-3}	$F\theta^2L^{-4}$	ML^{-3}
$DV\rho/\mu$	None	$MLF^{-1}\theta^{-2}$
$DV\rho/\mu' = DV\rho/\beta\mu$	None	None
$\Delta p/\rho V^2$	None	None	$F\theta^2M^{-1}L^{-1}$
$\Delta p\beta/\rho V^2$	None	None	None
Surface tension.....	$M\theta^{-2}$	FL^{-1}	FL^{-1}

† From E. W. Comings, *Ind. Eng. Chem.*, **32**:984 (1940).

per unit velocity gradient which indicates the dimensions $F\theta L^{-2}$, or it may be defined, as in the kinetic theory, as the rate of momentum transfer per unit area per unit velocity gradient which would make its dimensions $ML^{-1}\theta^{-1}$.) Within the $FML\theta$ system the dimensions of a quantity expressed in F, L , and θ may be changed to M, L , and θ by multiplying each F dimension by the dimensions of β , $ML\theta^{-2}F^{-1}$. The numerical value of the quantity may be converted by multiplying by the numerical value of β for the particular unit system used.

Definition of English Units. The actual size of the primary units has not been mentioned, and the above discussion is therefore independent of the amount chosen

for each primary unit. Some of the common English units for force and mass will be defined. The units for length and time are taken as feet and seconds, and their definitions do not need to be [given] here.

The English *absolute* or *dynamical unit system* uses as primary unit mass the avoirdupois pound or mass pound, which is defined in this country in terms of the United States prototype kilogram 20 as 0.4535924277 kg.³ The unit of force is a secondary unit, the poundal, and is the force required to give 1 mass lb unit acceleration, or

$$1 \text{ poundal} = \frac{1 \text{ mass lb}}{1} \times 1 \text{ ft/sec}^2 \quad (\text{A-5})$$

This definition makes the force of gravity on a mass pound numerically g_L poundals of force where the local acceleration of gravity is $g_L \text{ ft/sec}^2$.

The English *gravitational unit system* uses as a primary unit of force the standard force pound, which is defined as the force which will give the avoirdupois pound an acceleration of $g_0 \text{ ft/sec}^2$, where g_0 is the internationally adopted standard acceleration of gravity, 980.665 cm/sec² or, to the fourth decimal place, 32.1740 ft/sec². The unit of mass is a secondary unit, the slug, and is the amount of mass which will be accelerated 1 ft/sec² when acted upon by 1 standard force lb or

$$1 \times \frac{1 \text{ standard force lb}}{1 \text{ ft/sec}^2} = 1 \text{ slug} \quad (\text{A-6})$$

This makes the slug equal to 32.1740 mass lb.

The term "force pound" defined above and used hereafter is the standard gravitational force pound. This should be distinguished from the gravitational force pound which is defined so that the local force of gravity acts on 1 avoirdupois lb (one mass lb) with 1 gravitational force lb. This latter definition results in a force unit which is not a definite fixed quantity of force but varies with g_L from place to place so that the force of gravity acting on a body when measured in gravitational force pounds is always numerically equal to its mass in mass pounds. All scales or balances are calibrated⁴ locally against standard "weights" (standards of mass). (The weight of a body is variously interpreted as the mass of the body and also as the force of gravity acting on the body. It is therefore necessary to state definitely the units used in expressing a weight. Standard "weights" are, however, standards of mass.³) Then, the reading or weight is obtained in either mass-pound or gravitational force-pound units. The latter may be converted to standard force pounds by multiplying by the ratio g_L/g_0 , or

Local force of gravity (standard force lb)

$$= \frac{\text{weight (gravitational force lb)}}{g_0} \times g_L \quad (\text{A-7})$$

As shown later the weight in mass-pound units may be converted to standard force pounds by multiplying by g_L/g_c or

$$\text{Local force of gravity (standard force lb)} = \frac{\text{weight (mass lb)} \times g_L}{g_c}$$

³ Natl. Bur. Standards Letter Circ. 449 (1935).

⁴ W. L. DeBaufre, *Proc. Soc. Promotion Eng. Educ.*, **36**:655 (1928).

Another concept common among engineers⁵ is that mass is simply a ratio of weight (i.e., the force of gravity in standard force pounds) to g_L . Although the secondary unit of mass is not given a name in this case, this ratio is obviously the same as the mass measured in slugs.

The English *engineering-unit system* uses as a primary unit of force, the force pound, and as a primary unit of mass, the mass pound, both defined above. The relation between measurements in the four primary units is given by [Eq. (A-1)]:

$$\text{Force lb} = \frac{1}{\beta} \times \text{mass lb} \times \text{ft/sec}^2 \quad (\text{A-8})$$

β , therefore, [in this system] has the units (mass lb)(ft)/(force lb)(sec²) [and is designated as g_c]; and from the definition of a force pound as the force which will give 1 mass lb an acceleration of 32.1740 ft/sec², the numerical value of $[g_c]$ is 32.1740. $[g_c]$ is a dimensional constant and has nothing to do with the acceleration of gravity, either local g_L or standard g_0 , except that its numerical value happens to be equal to that of the standard acceleration of gravity, g_0 . This is in contradiction to numerous cases in the literature where the equivalent of $[g_c]$ is stated to be the acceleration of gravity.

[Table A-2] shows several sets of English units. In the absolute and gravitational unit systems, the poundal and the slug are secondary units; all the other units are primary. [Table A-2] also gives the relative size of the units which may be used to measure quantities of mass and force.¹

TABLE A-2. ENGLISH UNITS†

Name of system	Absolute	Gravitational	Engineering
Name of Quantity			
Mass.....	Mass pound	Slug (or gee pound)	Mass pound
Force.....	Poundal	Force pound	Force pound
Length.....	Foot	Foot	Foot
Time.....	Second	Second	Second
β	Unity	Unity	$(g_c), 32.1740 \frac{(\text{mass lb})(\text{ft})}{(\text{force lb})(\text{sec}^2)}$

$$1 \text{ mass lb} = \frac{1 \text{ force lb} \times 1 \text{ sec}^2}{32.1740 \times 1 \text{ ft}} = \frac{1 \text{ slug (or gee lb)}}{32.1740} = \frac{1 \text{ poundal} \times 1 \text{ sec}^2}{1 \text{ ft}}$$

$$1 \text{ force lb} = \frac{32.1740 \times 1 \text{ mass lb} \times 1 \text{ ft}}{1 \text{ sec}^2} = \frac{1 \text{ slug (or gee lb)} \times 1 \text{ ft}}{1 \text{ sec}^2} \\ = 32.1740 \text{ poundals}$$

† From E. W. Comings, *Ind. Eng. Chem.*, **34**:984 (1940).

A selected list of conversion factors is given in Table A-3. In converting from one system of units to another it is well to distinguish between the relative size of different units of the same dimensions and the relative numerical values of quantities measured in terms of these different units. The two viewpoints yield numerical conversion ratios such that one is the reciprocal of the other. For example a foot is 12 times an inch, but a length expressed in feet is $\frac{1}{12}$ the same

⁵ J. F. D. Smith, *J. Eng. Educ.*, **25**:604 (1934-35).

TABLE A-3. CONVERSION FACTORS†

1 cu ft = 7.48 gal = 28.4 liters
1 liter = 1,000.028 ± 0.004 cc
1 gal = 3,785.43449 cu cm = 231 cu in.
1 gal of water = 8.33 lb
1 lb mole (gas) at 32°F and 760 mm Hg = 359 cu ft
1 g mole (gas) at 0°C and 760 mm Hg = 22.4 liters
1 cu ft of water = 62.4 lb at room temperature
1 Btu = 778 ft-lb = 252.161 g-cal
1 kw hr = 3413 Btu
1 hp = 550 ft-lb force/sec = 33,000 ft-lb force/min = 745.578 watts
1 lb = 453.5924277 g = 7,000 grains
1 bbl = 42 gal
1 atm = 14.7 lb force/sq in. = 29.92 in. Hg = 34.0 ft of water = 760 mm Hg = 1 amagat = 1,013,250 dynes/sq cm
1 bar (also called "metric atmosphere") = 0.987 atm = 10 ⁶ dynes/sq cm
Specific gravity of Hg = 13.6 at room temperature ¹
Gas constant = 1,543 (ft)(lb-force)/(lb mole)(°F) = 10.73 (psi)(cu ft)/(°R) (lb mole) = 1.98719 ± 0.00013 g-cal/(g mole)(°C) = 1.99 Chu/(lb mole)(°C) = 1.99 Btu/(lb mole)(°F) = 0.7302 (atm)(cu ft)/(lb mole)(°R) = 82.0567 ± 0.0034 (cu cm)(atm)/(g mole)(°C)
1 g-cal (15°C) = 4.185 joules
1 faraday = 96,496 ± 7 coulombs/equivalent
<i>e</i> = 2.718
Avogadro's number = (6.0235 ± 0.0004) × 10 ²³ molecules/g mole
Composition of air: O ₂ = 20.9% by volume; N ₂ and inert = 79.1% by volume
Average molecular weight of air = 29
1 in. = 2.54000508 cm
1 ft = 30.4800610 cm
1 m = 3.28 ft
0°C = 273.160 ± 0.010°K = 32°F = 492°R
0°F = 459.63°R
ln <i>a</i> = 2.302585 log <i>a</i>
1 centipoise = 0.01 poise = 0.000672 (lb)/(sec)(ft)
<i>g</i> ₀ = 32.17 ft/sec ² = 980.665 cm/sec ²
<i>g</i> _c = 32.17 (lb mass)(ft)/(lb-force)(sec ²)
Numbers given to two, three, or four places are in most cases approximate values

† For additional factors, see F. D. Rossini, "Chemical Thermodynamics," John Wiley & Sons, Inc., New York, 1950.

length expressed in inches. Failure to distinguish between these two viewpoints sometimes leads to confusion and error. A useful rule to follow in converting units is as follows: *To convert a number representing a quantity expressed in one set of units to another set, substitute the equivalent units in the unit formula and carry out the indicated operations on the number.*

Example A-1. Convert 25 ft to inches

$$25(12 \text{ in.}) = 25 \times 12 \text{ in.} = 300 \text{ in.}$$

Example A-2. Convert viscosity expressed as pounds mass per foot \times second to pound-force units, for example, $0.0012 \text{ lb mass}/(\text{ft})(\text{sec})$.

$$0.0012 \times \frac{(\text{lb force})(\text{sec}^2)}{32.1740(\text{ft})} \times \frac{1}{(\text{ft})(\text{sec})}$$

$$\frac{0.0012}{32.1740} \frac{(\text{lb force})(\text{sec})}{\text{sq ft}} = 0.0000373 \frac{(\text{lb force})(\text{sec})}{\text{sq ft}}$$

APPENDIX B

VALUES FOR THE REDLICH AND KWONG EQUATION†

See Eqs. (8-20) to (8-23) and (8-136) to (8-139) and Figs. 8-47 to 8-49. The quantities in this table are dimensionless.

A^2/B	Parameter	$h=0.01$	0.02	0.04	0.06	0.08	0.10	0.15	0.20	0.25	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	$Bp (=z-1)$	0.0204	0.0417	0.0638	0.0870	0.1111	0.1765	0.2500	0.3333	0.4286	0.6667	1.0000	1.5000	2.333	4.000	9.000
	$\log \phi' (=w)$	0.0089	0.0181	0.0277	0.0378	0.0483	0.0767	0.1086	0.1449	0.1862	0.2897	0.434	0.652	1.014	1.738	3.910
	u	0.0000	0.000
1.0	Bp	0.0200	0.0401	0.0604	0.0810	0.1020	0.1570	0.2167	0.2833	0.359	0.553	0.833	1.275	2.045	3.642	8.575
	z	1.0008	1.0032	1.0072	1.0129	1.0202	1.0461	1.0833	1.1333	1.1978	1.3810	1.6667	2.125	2.922	4.556	9.526
	$\log \phi'$	0.0001	0.0007	0.0015	0.0028	0.0045	0.0103	0.0192	0.0316	0.0484	0.1011	0.1928	0.355	0.661	1.328	3.446
1.2	u	0.0172	0.0341	0.0506	0.0668	0.0828	0.1214	0.1584	0.1938	0.2278	0.2922	0.352	0.408	0.461	0.511	0.558
	w	0.0089	0.0184	0.0284	0.0390	0.0502	0.0807	0.1154	0.1548	0.1998	0.312	0.466	0.693	1.066	1.799	3.982
	Bp	0.0199	0.0398	0.0598	0.0798	0.1000	0.1530	0.2100	0.2732	0.3455	0.530	0.800	1.230	1.987	3.571	8.488
1.4	u	0.0206	0.0409	0.0608	0.0802	0.0994	0.1457	0.1900	0.2327	0.2733	0.351	0.423	0.490	0.553	0.613	0.669
	Bp	0.0199	0.0395	0.0591	0.0786	0.0984	0.1491	0.2033	0.2633	0.332	0.507	0.767	1.185	1.929	3.505	8.40
	z	0.0241	0.0477	0.0709	0.0936	0.1159	0.1700	0.2217	0.2713	0.319	0.409	0.493	0.572	0.645	0.715	0.781
1.5	u	0.0198	0.0394	0.0587	0.0781	0.0975	0.1471	0.2000	0.2582	0.325	0.495	0.750	1.163	1.900	3.467	8.36
	Bp	0.0910	0.0840	0.0789	0.0759	0.0748	0.0810	1.0000	1.033	1.083	1.238	1.500	1.938	2.715	4.333	9.29
	$\log \phi'$	-0.0041	-0.0078	-0.0111	-0.0139	-0.0162	-0.0205	-0.0218	-0.0208	-0.0144	0.0132	0.0778	0.2115	0.488	1.127	3.213
1.6	u	0.0258	0.0510	0.0760	0.1004	0.1242	0.1822	0.2374	0.2908	0.342	0.438	0.528	0.612	0.692	0.766	0.836
	w	0.0090	0.0185	0.0288	0.0397	0.0512	0.0828	0.1187	0.1599	0.2067	0.323	0.481	0.713	1.091	1.831	4.081
	Bp	0.0198	0.0392	0.0584	0.0775	0.0966	0.1452	0.1966	0.2533	0.318	0.484	0.734	1.140	1.872	3.430	8.32
1.8	u	0.0275	0.0545	0.0810	0.1070	0.1324	0.1943	0.2532	0.310	0.364	0.468	0.564	0.653	0.738	0.818	0.892
	Bp	0.0197	0.0389	0.0577	0.0763	0.0947	0.1413	0.1900	0.2433	0.304	0.461	0.700	1.095	1.815	3.360	8.23
	z	0.0310	0.0613	0.0912	0.1204	0.1490	0.2185	0.2850	0.349	0.410	0.526	0.634	0.735	0.830	0.919	1.004
2.0	Bp	0.0196	0.0386	0.0571	0.0751	0.0929	0.1373	0.1833	0.2332	0.2901	0.438	0.667	1.050	1.757	3.289	8.15
	z	0.0912	0.0648	0.0506	0.0389	0.0293	0.0156	0.0167	0.0333	0.0671	1.095	1.333	1.750	2.510	4.111	9.05
	$\log \phi'$	-0.0084	-0.0164	-0.0237	-0.0303	-0.0356	-0.0501	-0.0607	-0.0686	-0.0730	-0.0675	-0.0313	0.0725	0.318	0.925	2.98
2.2	u	0.0344	0.0682	0.1012	0.1336	0.1636	0.2428	0.3168	0.3876	0.456	0.584	0.704	0.816	0.922	1.022	1.116
	w	0.0090	0.0185	0.0286	0.0397	0.0504	0.0839	0.1214	0.1642	0.2132	0.335	0.497	0.734	1.117	1.862	4.055
	Bp	0.0195	0.0383	0.0564	0.0739	0.0911	0.1334	0.1766	0.2232	0.2762	0.416	0.634	1.005	1.698	3.218	8.16
2.4	u	0.0378	0.0749	0.1114	0.1471	0.1820	0.2670	0.348	0.426	0.501	0.643	0.775	0.898	1.014	1.124	1.226
	Bp	0.0195	0.0380	0.0558	0.0727	0.0893	0.1259	0.1700	0.2133	0.2626	0.392	0.600	0.960	1.632	3.148	7.98
	z	0.0113	0.0817	0.1215	0.1604	0.1987	0.2913	0.3800	0.4651	0.547	0.702	0.846	0.980	1.106	1.226	1.338
2.5	Bp	0.0194	0.0378	0.0554	0.0721	0.0884	0.1275	0.1666	0.2083	0.2562	0.381	0.583	0.937	1.613	3.110	7.93
	z	0.0714	0.0455	0.0223	0.0018	0.0838	0.8505	0.8330	0.8333	0.854	0.953	1.166	1.562	2.304	3.889	8.82
	$\log \phi'$	-0.0125	-0.0242	-0.0350	-0.0451	-0.0545	-0.0758	-0.1105	-0.1249	-0.1431	-0.1355	-0.062	0.151	0.152	0.725	2.717
2.6	u	0.0430	0.0852	0.1266	0.1672	0.2070	0.3036	0.396	0.484	0.570	0.731	0.880	1.020	1.152	1.276	1.394
	w	0.0091	0.0189	0.0286	0.0310	0.0531	0.0869	0.1254	0.1638	0.2214	0.345	0.511	0.754	1.142	1.803	4.060
	Bp	0.0194	0.0377	0.0548	0.0716	0.0875	0.1266	0.1633	0.2032	0.2486	0.370	0.567	0.915	1.585	3.075	7.89

2.8	u	0.0447	0.0885	0.1317	0.1738	0.2152	0.3157	0.412	0.504	0.592	0.710	0.902	1.104	1.306	1.508	1.710	1.912	2.114	2.316	2.518	2.720	2.922	3.124	3.326	3.528	3.730	3.932	4.134	4.336	4.538	4.740	4.942	5.144	5.346	5.548	5.750	5.952	6.154	6.356	6.558	6.760	6.962	7.164	7.366	7.568	7.770	7.972	8.174	8.376	8.578	8.780	8.982	9.184	9.386	9.588	9.790	9.992	10.194	10.396	10.598	10.800	11.002	11.204	11.406	11.608	11.810	12.012	12.214	12.416	12.618	12.820	13.022	13.224	13.426	13.628	13.830	14.032	14.234	14.436	14.638	14.840	15.042	15.244	15.446	15.648	15.850	16.052	16.254	16.456	16.658	16.860	17.062	17.264	17.466	17.668	17.870	18.072	18.274	18.476	18.678	18.880	19.082	19.284	19.486	19.688	19.890	20.092	20.294	20.496	20.698	20.900	21.102	21.304	21.506	21.708	21.910	22.112	22.314	22.516	22.718	22.920	23.122	23.324	23.526	23.728	23.930	24.132	24.334	24.536	24.738	24.940	25.142	25.344	25.546	25.748	25.950	26.152	26.354	26.556	26.758	26.960	27.162	27.364	27.566	27.768	27.970	28.172	28.374	28.576	28.778	28.980	29.182	29.384	29.586	29.788	29.990	30.192	30.394	30.596	30.798	30.999	31.201	31.403	31.605	31.807	32.009	32.211	32.413	32.615	32.817	33.019	33.221	33.423	33.625	33.827	34.029	34.231	34.433	34.635	34.837	35.039	35.241	35.443	35.645	35.847	36.049	36.251	36.453	36.655	36.857	37.059	37.261	37.463	37.665	37.867	38.069	38.271	38.473	38.675	38.877	39.079	39.281	39.483	39.685	39.887	40.089	40.291	40.493	40.695	40.897	41.099	41.301	41.503	41.705	41.907	42.109	42.311	42.513	42.715	42.917	43.119	43.321	43.523	43.725	43.927	44.129	44.331	44.533	44.735	44.937	45.139	45.341	45.543	45.745	45.947	46.149	46.351	46.553	46.755	46.957	47.159	47.361	47.563	47.765	47.967	48.169	48.371	48.573	48.775	48.977	49.179	49.381	49.583	49.785	49.987	50.189	50.391	50.593	50.795	50.997	51.199	51.401	51.603	51.805	52.007	52.209	52.411	52.613	52.815	53.017	53.219	53.421	53.623	53.825	54.027	54.229	54.431	54.633	54.835	55.037	55.239	55.441	55.643	55.845	56.047	56.249	56.451	56.653	56.855	57.057	57.259	57.461	57.663	57.865	58.067	58.269	58.471	58.673	58.875	59.077	59.279	59.481	59.683	59.885	60.087	60.289	60.491	60.693	60.895	61.097	61.299	61.501	61.703	61.905	62.107	62.309	62.511	62.713	62.915	63.117	63.319	63.521	63.723	63.925	64.127	64.329	64.531	64.733	64.935	65.137	65.339	65.541	65.743	65.945	66.147	66.349	66.551	66.753	66.955	67.157	67.359	67.561	67.763	67.965	68.167	68.369	68.571	68.773	68.975	69.177	69.379	69.581	69.783	69.985	70.187	70.389	70.591	70.793	70.995	71.197	71.399	71.601	71.803	72.005	72.207	72.409	72.611	72.813	73.015	73.217	73.419	73.621	73.823	74.025	74.227	74.429	74.631	74.833	75.035	75.237	75.439	75.641	75.843	76.045	76.247	76.449	76.651	76.853	77.055	77.257	77.459	77.661	77.863	78.065	78.267	78.469	78.671	78.873	79.075	79.277	79.479	79.681	79.883	80.085	80.287	80.489	80.691	80.893	81.095	81.297	81.499	81.701	81.903	82.105	82.307	82.509	82.711	82.913	83.115	83.317	83.519	83.721	83.923	84.125	84.327	84.529	84.731	84.933	85.135	85.337	85.539	85.741	85.943	86.145	86.347	86.549	86.751	86.953	87.155	87.357	87.559	87.761	87.963	88.165	88.367	88.569	88.771	88.973	89.175	89.377	89.579	89.781	89.983	90.185	90.387	90.589	90.791	90.993	91.195	91.397	91.599	91.801	92.003	92.205	92.407	92.609	92.811	93.013	93.215	93.417	93.619	93.821	94.023	94.225	94.427	94.629	94.831	95.033	95.235	95.437	95.639	95.841	96.043	96.245	96.447	96.649	96.851	97.053	97.255	97.457	97.659	97.861	98.063	98.265	98.467	98.669	98.871	99.073	99.275	99.477	99.679	99.881	100.083	100.285	100.487	100.689	100.891	101.093	101.295	101.497	101.699	101.901	102.103	102.305	102.507	102.709	102.911	103.113	103.315	103.517	103.719	103.921	104.123	104.325	104.527	104.729	104.931	105.133	105.335	105.537	105.739	105.941	106.143	106.345	106.547	106.749	106.951	107.153	107.355	107.557	107.759	107.961	108.163	108.365	108.567	108.769	108.971	109.173	109.375	109.577	109.779	109.981	110.183	110.385	110.587	110.789	110.991	111.193	111.395	111.597	111.799	112.001	112.203	112.405	112.607	112.809	113.011	113.213	113.415	113.617	113.819	114.021	114.223	114.425	114.627	114.829	115.031	115.233	115.435	115.637	115.839	116.041	116.243	116.445	116.647	116.849	117.051	117.253	117.455	117.657	117.859	118.061	118.263	118.465	118.667	118.869	119.071	119.273	119.475	119.677	119.879	120.081	120.283	120.485	120.687	120.889	121.091	121.293	121.495	121.697	121.899	122.101	122.303	122.505	122.707	122.909	123.111	123.313	123.515	123.717	123.919	124.121	124.323	124.525	124.727	124.929	125.131	125.333	125.535	125.737	125.939	126.141	126.343	126.545	126.747	126.949	127.151	127.353	127.555	127.757	127.959	128.161	128.363	128.565	128.767	128.969	129.171	129.373	129.575	129.777	129.979	130.181	130.383	130.585	130.787	130.989	131.191	131.393	131.595	131.797	131.999	132.201	132.403	132.605	132.807	133.009	133.211	133.413	133.615	133.817	134.019	134.221	134.423	134.625	134.827	135.029	135.231	135.433	135.635	135.837	136.039	136.241	136.443	136.645	136.847	137.049	137.251	137.453	137.655	137.857	138.059	138.261	138.463	138.665	138.867	139.069	139.271	139.473	139.675	139.877	140.079	140.281	140.483	140.685	140.887	141.089	141.291	141.493	141.695	141.897	142.099	142.301	142.503	142.705	142.907	143.109	143.311	143.513	143.715	143.917	144.119	144.321	144.523	144.725	144.927	145.129	145.331	145.533	145.735	145.937	146.139	146.341	146.543	146.745	146.947	147.149	147.351	147.553	147.755	147.957	148.159	148.361	148.563	148.765	148.967	149.169	149.371	149.573	149.775	149.977	150.179	150.381	150.583	150.785	150.987	151.189	151.391	151.593	151.795	151.997	152.199	152.401	152.603	152.805	153.007	153.209	153.411	153.613	153.815	154.017	154.219	154.421	154.623	154.825	155.027	155.229	155.431	155.633	155.835	156.037	156.239	156.441	156.643	156.845	157.047	157.249	157.451	157.653	157.855	158.057	158.259	158.461	158.663	158.865	159.067	159.269	159.471	159.673	159.875	160.077	160.279	160.481	160.683	160.885	161.087	161.289	161.491	161.693	161.895	162.097	162.299	162.501	162.703	162.905	163.107	163.309	163.511	163.713	163.915	164.117	164.319	164.521	164.723	164.925	165.127	165.329	165.531	165.733	165.935	166.137	166.339	166.541	166.743	166.945	167.147	167.349	167.551	167.753	167.955	168.157	168.359	168.561	168.763	168.965	169.167	169.369	169.571	169.773	169.975	170.177	170.379	170.581	170.783	170.985	171.187	171.389	171.591	171.793	171.995	172.197	172.399	172.601	172.803	173.005	173.207	173.409	173.611	173.813	174.015	174.217	174.419	174.621	174.823	175.025	175.227	175.429	175.631	175.833	176.035	176.237	176.439	176.641	176.843	177.045	177.247	177.449	177.651	177.853	178.055	178.257	178.459	178.661	178.863	179.065	179.267	179.469	179.671	179.873	180.075	180.277	180.479	180.681	180.883	181.085	181.287	181.489	181.691	181.893	182.095	182.297	182.499	182.701	182.903	183.105	183.307	183.509	183.711	183.913	184.115	184.317	184.519	184.721	184.923	185.125	185.327	185.529	185.731	185.933	186.135	186.337	186.539	186.741	186.943	187.145	187.347	187.549	187.751	187.953	188.155	188.357	188.559	188.761	188.963	189.165	189.367	189.569	189.771	189.973	190.175	190.377	190.579	190.781	190.983	191.185	191.387	191.589	191.791	191.993	192.195	192.397	192.599	192.801	193.003	193.205	193.407	193.609	193.811	194.013	194.215	194.417	194.619	194.821	195.023	195.225	195.427	195.629	195.831	196.033	196.235	196.437	196.639	196.841	197.043	197.245	197.447	197.649	197.851	198.053	198.255	198.457	198.659	198.861	199.063	199.265	199.467	199.669	199.871	200.073	200.275	200.477	200.679	200.881	201.083	201.285	201.487	201.689	201.891	202.093	202.295	202.497	202.699	202.901	203.103	203.305	203.507	203.709	203.911	204.113	204.315	204.517	204.719	204.921	205.123	205.325	205.527	205.729	205.931	206.133	206.335	206.537	206.739	206.941	207.143	207.345	207.547	207.749	207.951	208.153	208.355	208.557	208.759	208.961	209.163	209.365	209.567	209.769	209.971	210.173	210.375	210.577	210.779	210.981	211.183	211.385	211.587	211.789	211.991	212.193	212.395	212.597	212.799	213.001	213.203	213.405	213.607	213.809	214.011	214.213	214.415	214.617	214.819	215.021	215.223	215.425	215.627	2
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APPENDIX B (Continued)

A^2/B	Parameter	$h = 0.01$	0.02	0.04	0.06	0.08	0.10	0.15	0.20	0.25	0.3	0.4	0.5	0.6	0.7	0.8	0.9
7	Bp	0.0094	0.0177	0.0309	0.0406	0.0455	0.0475										
	z	0.9407	0.8832	0.7725	0.6677	0.5685	0.4748										
	$\log \phi'$	-0.0251	-0.0482	-0.0882	-0.1189	-0.1398	-0.1484										
	u	0.0504	0.1204	0.2384	0.354	0.468	0.579										
8	w	0.0044	0.0095	0.0204	0.0328	0.0465	0.0617										
	Bp	0.0093	0.0172	0.0294	0.0367	0.0396	0.0384										
	z	0.9309	0.8635	0.7341	0.6110	0.495	0.384										
	$\log \phi'$	-0.0291	-0.0556	-0.0997	-0.1304	-0.1445	-0.1377										
9	u	0.0692	0.1376	0.2724	0.405	0.535	0.662										
	w	0.0046	0.0095	0.0207	0.0335	0.0481	0.0634										
	Bp	0.0092	0.0169	0.0278	0.0332	0.0336	0.0293	0.0005									
	z	0.9210	0.8439	0.6957	0.554	0.420	0.293	0.003									
10	$\log \phi'$	-0.0331	-0.0627	-0.1101	-0.139	-0.140	-0.101	1.544									
	u	0.0778	0.1548	0.3064	0.456	0.602	0.744	1.092									
	w	0.0046	0.0096	0.0210	0.034	0.049	0.065	0.113									
	Bp	0.0091	0.0165	0.0263	0.0299	0.0299	0.0299										
11	z	0.9110	0.8243	0.6571	0.4978	0.341	0.191										
	$\log \phi'$	-0.0371	-0.0696	-0.1191	-0.1414	-0.1414	-0.1414										
	u	0.0864	0.1720	0.341	0.506	0.664	0.822										
	w	0.0045	0.0097	0.0214	0.0350	0.049	0.064										
11	Bp	0.0090	0.0161	0.0247	0.0265	0.0218	0.0111										
	z	0.9012	0.8046	0.6187	0.441	0.272	0.111										
	$\log \phi'$	-0.0409	-0.0818	-0.1267	-0.139	-0.080	0.159										
	u	0.0950	0.1892	0.375	0.557	0.735	0.910										
	w	0.0046	0.0097	0.0217	0.035	0.052	0.067										

APPENDIX C

CONSTANTS FOR EQUATIONS OF STATE

TABLE C-1. CONSTANTS FOR VAN DER WAALS' EQUATION†
[See Eq. (8-5)]

Gas	$a,$ (liter ²)(atm)/ mole ²	$b,$ liters/mole $\times 10^{-2}$	Gas	$a,$ (liter ²)(atm)/ mole ²	$b,$ liters/mole $\times 10^{-2}$
Acetylene.....	4.40	5.15	Hydrogen chloride....	3.68	4.09
Ammonia.....	4.17	3.72	Hydrogen cyanide....	10.8	8.25
Argon.....	1.35	3.23	Hydrogen iodide.....	7.72	5.31
Benzene.....	18.0	11.5	Hydrogen sulfide.....	4.43	4.30
<i>n</i> -Butane.....	14.5	12.3	Methane.....	2.26	4.30
Carbon dioxide.....	3.60	4.28	Methanol.....	9.54	6.71
Carbon monoxide....	1.49	4.00	Methyl chloride.....	7.47	6.51
Chlorine.....	6.50	5.64	Nitric oxide.....	1.34	2.80
Cyanogen.....	7.68	6.93	Nitrogen.....	1.39	3.92
Ethane.....	5.46	6.47	Nitrous oxide.....	3.79	4.43
Ethyl ether.....	17.4	13.5	Oxygen.....	1.36	3.19
Ethylene.....	4.47	5.73	Propane.....	8.66	8.47
Helium.....	0.034	2.38	Propylene.....	8.38	8.30
Hydrogen.....	0.245	2.67	Sulfur dioxide.....	6.72	5.65
Hydrogen bromide....	4.46	4.44	Water.....	5.46	3.30

† From S. Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Company, Inc., New York, (1947).

TABLE C-2. CONSTANTS FOR THE BEATTIE-BRIDGEMAN EQUATION

$$p = \frac{RT(1 - \epsilon)}{v^2} (v + B) - \frac{A}{v^2}$$

Compound	Formula	Mol. wt.	Temp, °C		Max. pressure, atm.	A ₀	a	B ₀	b	C	Ref.
			Min.	Max.							
Isobutane.....	C ₄ H ₁₀	56.0616	150	275	250	16.9600	0.10860	0.24200	0.08750	250 × 10 ⁴	1
n-Butane.....	C ₄ H ₁₀	58.077	150	300	350	17.7940	0.12161	0.24620	0.09423	350	2
n-Heptane.....	C ₇ H ₁₆	100.1248	30	250	350	54.520	0.20066	0.70816	0.19179	400	3
Propane.....	C ₃ H ₈	44.0616	97	275	300	11.9200	0.07321	0.18100	0.04293	120	4
Ammonia.....	NH ₃	17.0311	75	325	130	2.3930	0.17031	0.03415	0.19112	476.87	5
Helium.....	He	4.003	-252	400	102	0.0216	0.05984	0.01400	0.0	0.004	6
Neon.....	Ne	20.183	-217	400	106	0.2125	0.02196	0.02060	0.0	0.101	6
Argon.....	A	39.944	-150	400	114	1.2907	0.00506	0.03931	0.0	5.99	6
Hydrogen.....	H ₂	2.0160	-244	200	103	0.1975	0.02096	0.02096	-0.04359	0.0504	6
Nitrogen.....	N ₂	28.016	-149	400	134	1.3445	0.02617	0.05046	-0.00691	4.2	6
Nitrogen†.....	N ₂	0	200	213	1.1440	0.01788	0.04314	-0.01608	5.60	6
Oxygen.....	O ₂	32.0000	-117	100	103	1.4911	0.02562	0.04624	-0.004208	4.80	6
Air.....	-145	200	177	1.3012	0.01931	0.04611	-0.01101	4.34	6
Carbon dioxide.....	CO ₂	44.010	0	100	111	5.0065	0.07132	0.10476	0.07235	66.0	6
Methane.....	CH ₄	16.043	0	200	243	2.2769	0.01855	0.05587	-0.01587	12.83	6
Ethyl ether.....	(C ₂ H ₅) ₂ O	74.044	150	325	90	31.278	0.12426	0.45446	0.11954	33.33	6

† $A = A_0 \left(1 - \frac{a}{v} \right)$; $B = B_0 \left(1 - \frac{b}{v} \right)$; $\epsilon = \frac{c}{vT^3}$; p in normal atm; v in liters/g mole; T in °K; $R = 0.08206$ (l)(atm)/(g mole)(°K)

‡ Constants for Smith and Taylor's data alone.

1. J. A. Beattie, H. C. Ingersoll, and W. H. Stockmayer, *J. ACS*, **64**:548 (1942).
2. J. A. Beattie, G. L. Sinaud, and G. J. Su, *ibid.*, **61**:26 (1939).
3. L. B. Smith, J. A. Beattie, and W. C. Kay, *ibid.*, **59**:1587 (1937).
4. J. A. Beattie, W. C. Kay, and J. Kaminsky, *ibid.*, **59**:1589 (1937).
5. J. A. Beattie and C. K. Lawrence, *ibid.*, **52**:6 (1930).
6. J. A. Beattie and O. C. Bridgeman, *ibid.*, **50**:3133 (1928).
7. L. B. Smith and R. S. Taylor, *ibid.*, **45**:2107 (1923); and **48**:3122 (1926).

TABLE C-3. CONSTANTS FOR THE BENEDICT-WEBB-RUBIN EQUATION††
[See Eq. (8-30)]

Substance	Methane	Ethylene	Ethane	Propylene	Propane	i-Butane	i-Butylene	n-Butane	i-Pentane	n-Pentane	n-Hexane	n-Heptane
Molecular wt	16.031	28.031	30.047	42.047	44.062	58.078	56.062	58.078	72.094	72.094	86.109	100.125
B_0	0.682401	0.891980	1.00554	1.36263	1.55884	2.20329	1.85858	1.99211	2.56386	2.51096	2.84835	3.18782
A_0	6.995 25	12.593 6	15.670 7	23.049 2	25.915 4	38.587 4	33.762 9	38.029. 6	4.825 36	45.928. 8	5.443. 4	66.070 6
$C_0 \times 10^6$	275.763	1,602.28	2,194 27	5,365.97	6,209.93	10,384 7	11,329. 6	12,130 5	21,336 7	25,917. 2	40,556. 2	57,984 0
b	0.867325	2.20678	2.85393	4.79997	5.77355	10.8890	8.93375	10.2636	17.1441	17.1441	28.0032	38.9917
a	2,984 12	15,645. 5	20,850. 2	46,758. 6	57,248 0	117,047	102,351.	113,705	226,902	246,148	429,901	626,106
$c \times 10^6$	498 106	4,133 60	6,413 14	20,083. 0	25,247 8	55,977. 7	53,807. 2	61,925. 6	136,025	161,306	296,077	483,427
$\alpha \times 10^3$	511 172	731 661	1,000 44	2,495 77	2,495 77	4,414. 96	3,744. 17	4,526. 93	6,987. 77	7,439. 92	11,553. 9	17,905. 6
$\gamma = 10^2$	153 961	236 844	302 790	469 325	564 524	872 447	759 401	872 447	1,188. 07	1,218. 86	1,711 15	2,309 42
$A_0^{1/2}$	83 6376	112 221	125 183	151 820	160 983	196 437	183 747	195 012	219. 667	214. 310	233 331	257. 042
$C_0^{1/2} \times 10^{-3}$	16 6061	40 0285	46 8430	73 2528	78 8031	101 995	106 441	110 139	146. 071	160. 988	201. 386	240 799
$b^{1/2}$	0.953644	1.30193	1.41845	1.68686	1.79396	2.21647	2.07497	2.17320	2.57853	2.57853	3.03671	3.39097
$a^{1/2}$	14 3970	25 0109	27 5235	36 0264	38 5408	48 9165	46 7620	48 4464	60. 9929	62. 6707	75 4726	85 5494
$c^{1/2}$	7.92684	16 0486	18 5788	27 1813	29 3360	38 2530	37 7521	39 5625	51 4281	54 4349	66 4492	78 4822
$\alpha^{1/2} \times 10$	7.99567	9 01094	10 0015	12 3270	13 5644	16 4050	15 5281	16 5425	19 1181	19 5220	22.6070	26 1616
$\gamma^{1/2} \times 10$	12 4082	15 3897	17 4009	21 6640	23 7597	29 5372	27 5573	29 5372	34 4683	34 9122	41 3660	48 0564

† From M. Benedict, G. B. Webb, L. C. Rubin, and L. Friend, *Chem. Eng. Progr.*, **47**:419 (1951).

†† p in psia; d in lb mole/cu ft; T in $^{\circ}R$ ($^{\circ}F + 459.63$); $R = 10.7335$ (lb)(cu ft)/(sq in.)(lb mole)($^{\circ}R$).

APPENDIX D

PROPERTIES OF GASES, LIQUIDS, AND SOLIDS

TABLE D-1. p AND pV VALUES FOR HYDROGEN†

p = int atm; pV = 0.99939 at 0°C, 0 atm‡; pV = 1.00000 at 0°C, 1 atm

0°C			25°C			50°C			75°C			100°C			125°C			150°C		
p	pV		p	pV		p	pV		p	pV		p	pV		p	pV		p	pV	
9.1670	1.00513		10.0061	1.09714		10.8467	1.18931		11.6872	1.28146		12.5279	1.37364		13.3675	1.46570		14.2074	1.55780	
11.3642	1.00643		12.4053	1.09863		13.4477	1.19095		14.4919	1.28342		15.5339	1.37570		16.5746	1.46787		17.6167	1.56016	
14.1903	1.00816		15.4915	1.10061		16.7939	1.19314		18.0999	1.28592		19.4015	1.37840		20.7020	1.47079		22.0038	1.56328	
17.7971	1.01057		19.4290	1.10323		21.0642	1.19608		22.6995	1.28894		24.3336	1.38173		25.9676	1.47451		27.6024	1.56734	
22.0064	1.01319		24.0276	1.10625		26.0515	1.19943		28.0767	1.29267		30.0838	1.38572		32.1198	1.47882		34.1430	1.57197	
26.9851	1.01631		29.4685	1.10984		31.9519	1.20337		34.4345	1.29687		36.9192	1.39045		39.4029	1.48399		41.8842	1.57744	
27.3136	1.01621		29.8280	1.10976		32.3484	1.20353		34.8687	1.29730		37.3815	1.39079		39.8930	1.48423		42.4071	1.57777	
31.8598	1.01951		34.7926	1.11336		37.7282	1.20730		40.6639	1.30124		43.5986	1.39515		46.5326	1.48904		49.4661	1.58291	
33.1182	1.01992		36.1709	1.11393		39.2313	1.20818		42.2836	1.30218		45.3401	1.39631		48.3912	1.49027		51.4444	1.58430	
36.6671	1.02257		40.0499	1.11691		43.4342	1.21129		46.8131	1.30552		50.1930	1.39978		53.5726	1.49403		56.9565	1.58840	
40.5286	1.02479		44.2671	1.11932		48.0178	1.21416		51.7595	1.30877		55.5059	1.40350		59.2444	1.49803		62.9829	1.59256	
49.8423	1.03075		54.4530	1.12610		59.0734	1.22165		63.6850	1.31702		68.2996	1.41245		72.9006	1.50760		77.5084	1.60289	
61.0457	1.03811		66.7028	1.13431		72.3698	1.23068		78.0344	1.32701		83.6944	1.42326		89.3396	1.51926		94.9943	1.61542	
75.7197	1.04769		82.7598	1.14510		89.8122	1.24268		96.8610	1.34021		103.8932	1.43751		110.9101	1.53460		117.9336	1.63178	
94.2404	1.06001		103.0198	1.15876		111.8241	1.25779		120.6248	1.35678		129.3980	1.45546		138.1542	1.55395		146.9061	1.65239	
118.3952	1.07624		129.4973	1.17716		140.6037	1.27812		151.7013	1.37900		162.7560	1.47949		173.7789	1.57969		184.8072	1.67994	
145.4123	1.09470		159.0808	1.19760		172.7719	1.30067		186.4510	1.40365		200.0903	1.50633		213.7004	1.60879		227.2866	1.71107	
147.2250	1.09565		161.1137	1.19901		174.9890	1.30227		188.8441	1.40538		202.6294	1.50797		216.3743	1.61026		230.0978	1.71239	

† From A. Michels and M. Goudeket, *Physica*, 8:347 (1941).

‡ J. H. Perry, editor, "Chemical Engineers' Handbook," 3rd ed., p. 205, McGraw-Hill Book Company, Inc., New York, 1950.

TABLE D-1. p AND pV VALUES FOR HYDROGEN (Continued)

0°C			25°C			50°C			75°C			100°C			125°C			150°C									
p	pV	p	pV	p	pV	p	pV	p	pV	p	pV	p	pV	p	pV	p	pV	p	pV								
165	0824	1	10826	180	6439	1	21273	196	2203	1	31730	211	7788	1	42175	227	2926	1	52590	242	7572	1	62972	258	2085	1	73345
186	4162	1	12315	204	0196	1	22921	221	6513	1	33544	239	2497	1	44147	256	7967	1	54719	274	2690	1	65246	291	8376	1	75831
208	2018	1	13854	227	9424	1	24649	247	6683	1	35436	267	3412	1	46194	286	9318	1	56907	306	4327	1	67571	325	9282	1	78233
209	6317	1	13937	229	5025	1	24737	249	3678	1	35534	269	1613	1	46292	288	8518	1	56994	308	5828	1	67718	328	2163	1	78389
237	768	1	15945	260	361	1	26962	282	927	1	37966	305	423	1	48936	327	782	1	59839	350	118	1	70731	372	409	1	81601
270	235	1	18261	295	955	1	29517	321	640	1	40757	347	230	1	51956	372	668	1	63088	398	050	1	74196	423	366	1	85275
306	071	1	20826	335	253	1	32346	364	361	1	43837	393	353	1	55282	422	211	1	66674	450	927	1	78010	479	617	1	89336
344	234	1	23577	377	115	1	35381	409	860	1	47136	442	479	1	58846	474	889	1	70481	507	196	1	82079	539	439	1	93654
386	876	1	26683	423	792	1	38771	460	570	1	50814	497	155	1	62794	533	558	1	74714	569	819	1	86588	605	926	1	98411
434	919	1	30182	476	385	1	42594	517	655	1	54947	558	754	1	67249	599	559	1	79463	640	214	1	91632	680	705	2	03752
460	589	1	32054	504	542	1	44655	548	355	1	57217	591	854	1	69688	634	976	1	82051	677	886	1	94354	720	642	2	06612
483	075	1	33700	529	048	1	46424	574	794	1	59085	620	308	1	71682	665	487	1	84186	710	467	1	96635	755	266	2	09034
538	965	1	37779	590	231	1	50884	641	269	1	63931	691	874	1	76868	742	017	1	89686	791	906	2	02439	841	544	2	15129
629	401	1	44368	688	881	1	58011	748	161	1	71609	806	765	1	85051	864	846	1	98373	922	600	2	11620	979	944	2	24774
734	761	1	52001	803	665	1	66255	872	181	1	80429	939	794	1	94416	1006	841	2	08286	1073	415	2	22058	1139	597	2	35749
853	513	1	60530	932	670	1	75418	1011	215	1	90191	1088	953	2	04812	1165	686	2	19244	1241	860	2	33571	1317	525	2	47802
994	395	1	70550	1085	164	1	86118	1175	227	2	01564	1263	920	2	16776	1351	739	2	31838	1438	899	2	46787	1525	027	2	61559
1162	970	1	8227	1267	440	1	98645	1370	693	2	14828	1472	452	2	30776	1572	687	2	46486	1672	212	2	62094	1771	008	2	77569
1290	292	1	91006	1403	949	2	07831	1516	249	2	24455	1627	291	2	40893	1736	733	2	57094	1845	020	2	73124	1952	421	2	89023
1343	355	1	94609	1461	431	2	11714	1578	059	2	28610	1692	788	2	45230	1806	088	2	61644	1918	181	2	77883	2029	260	2	93974
1610	045	2	12366	1746	648	2	30384	1881	795	2	48210	2014	554	2	65721	2145	486	2	82991	2275	629	3	00157	2406	265	3	17388
2017	419	2	38561	2180	149	2	57804	2342	229	2	76970	2500	486	2	95684	2656	908	3	14186	2812	518	3	32582	2970	014	3	51206
2541	940	2	70692	2736	183	2	91377	2932	304	3	12262																

TABLE D-2. pV VALUES OF CARBON MONOXIDE IN AMAGAT UNITS†
1 Amagat unit of $pV = 2,269.7$ joules/mole or 542.27 cal/mole

p , int. atm	0°C	25°C	50°C	75°C	100°C	125°C	150°C
0	1.00062	1.09220	1.18379	1.27537	1.36695	1.45853	1.55011
1	1.00000	1.09183	1.18363	1.27541	1.36715	1.45887	1.55056
50	0.97749	1.08132	1.18291	1.28294	1.38165	1.47928	1.57607
100	0.97195	1.08536	1.19476	1.30118	1.40527	1.50750	1.60854
200	1.01822	1.13873	1.25528	1.36842	1.47857	1.58636	1.69246
300	1.11883	1.23675	1.35279	1.46680	1.57835	1.68798	1.79604
400	1.24520	1.35862	1.47184	1.58430	1.69531	1.80474	1.91315
600	1.52175	1.62905	1.73725	1.84585	1.95410	2.06164	2.16898
800	1.80239	1.90678	2.01232	2.11849	2.22461	2.33039	2.43655
1,000	2.07808	2.18159	2.28603	2.39099	2.49601	2.60070	2.70592
1,200	2.34732	2.45095	2.55514	2.65985	2.76430	2.86858	2.97331
1,500	2.73965	2.84417	2.94920	3.05414	3.15883	3.26316	3.36777
2,000	3.36703	3.47367	3.58093	3.68761	3.79404	3.89981	4.00523
2,500	(3.9647)	4.07572	4.18587	4.29543	4.40412	4.51175	4.61860
3,000	(4.5410)	4.65586	(4.7694)	(4.8818)	(4.9930)	5.10309	(5.2109)

† From A. Michels, R. J. Lunbeck, and G. J. Wolkers, *Appl. Sci. Res.*, **A2**:345 (1951).

TABLE D-3. pV VALUES OF NITROGEN IN AMAGAT UNITS†
1 Amagat unit of $pV = 2,270.1$ joules/mole

p , int. atm	-125°C	-100°C	-75°C	-50°C	-25°C	0°C	25°C	50°C	75°C	100°C	125°C	150°C
0	0.5247	0.6343	0.7258	0.8174	0.9089	1.00045	1.09202	1.18358	1.27515	1.36671	1.45828	1.54985
1	0.5384	0.6312	0.7236	0.8162	0.9080	1.00000	1.09181	1.18357	1.27529	1.36700	1.45869	1.55036
3	0.5306	0.6252	0.7196	0.8137	0.9062	0.99907	1.09141	1.18356	1.27560	1.36760	1.45952	1.55140
5	0.5220	0.6194	0.7156	0.8112	0.9046	0.99823	1.09103	1.18357	1.27591	1.36821	1.46037	1.55245
10	0.5030	0.6058	0.7060	0.8052	0.9007	0.99616	1.09016	1.18366	1.27678	1.36979	1.46252	1.55510
30	0.4250	0.5556	0.6726	0.7834	0.8879	0.98934	1.08789	1.18507	1.28119	1.37684	1.47179	1.56630
50	0.3425	0.5146	0.6456	0.7654	0.8782	0.98558	1.08767	1.18829	1.28720	1.38519	1.48218	1.57847
100	0.2846	0.4482	0.6091	0.7448	0.8705	0.98470	1.09677	1.20443	1.30949	1.41215	1.51348	1.61358
200	0.4378	0.5335	0.6555	0.7862	0.9151	1.03616	1.15449	1.26904	1.38033	1.48894	1.59556	1.70074
300	0.5945	0.6809	0.7843	0.8988	1.0178	1.13445	1.25150	1.36612	1.47862	1.58890	1.69762	1.80477
400	0.7465	0.8310	0.9278	1.0341	1.1459	1.25664	1.36994	1.48250	1.59394	1.70390	1.81276	1.92045
600	1.0356	1.1216	1.2155	1.3160	1.4214	1.52501	1.63248	1.74068	1.84884	1.95672	2.06418	2.17101
800	1.3096	1.3990	1.4940	1.5939	1.6977	1.79833	1.90294	2.00865	2.11473	2.22082	2.32681	2.43271
1,000	1.5727	1.6656	1.7628	1.8638	1.9679	2.06756	2.17098	2.27560	2.38078	2.48584	2.59105	2.69623
1,200	1.8270	1.9234	2.0232	2.1258	2.2312	2.33094	2.43418	2.53856	2.64347	2.74806	2.85289	2.95798
1,500	2.1957	2.2971	2.4006	2.5065	2.6143	2.71533	2.81933	2.92407	3.02917	3.13403	3.23888	3.34424
2,000	2.7836	2.8925	3.0025	3.1139	3.2264	3.33110	3.43838	3.54444	3.65059	3.75715	3.86323	3.96947
2,500	3.3468	3.4622	3.5782	3.6949	3.8121	3.92238	4.03422	4.14175	4.24956	4.35848	4.46714	4.57447
3,000	3.891	4.0123	4.1336	4.2552	4.3775	4.49396	4.61096	4.72211	4.83159	4.94261	5.05446	5.16389
3,500	4.9256	5.04959	5.17154	5.28601	5.39878	5.51258	5.62713	5.73933
4,000	5.5498	5.59163	5.71847	5.83700	5.95283	6.06996	6.187	6.30243
4,500	5.9818	6.12237	6.25365	6.37638	6.49577	6.61642	6.737	6.85489
5,000	6.64310	6.77928	6.90566	7.02852	7.15292	7.276	7.39735
5,500	7.167	7.29490	7.426	7.55225	7.68050	7.807	7.93113
6,000	7.682	7.810	7.938	8.06779	8.19999	8.332	8.45888

† From R. J. Lunbeck, A. Michels, and G. J. Wolkers, *Appl. Sci. Res.*, **A3**:197 (1952).

TABLE D-4. pV VALUES IN AMAGAT UNITS FOR ETHYLENE†

p	0°C	25°C	50°C	75°C	100°C	125°C	150°C
0	1.00758	1.09980	1.19202	1.28424	1.37646	1.46868	1.56089
1	1.00000	1.09347	1.18670	1.27975	1.37264	1.46542	1.55810
50	0.17403	0.68120	0.88679	1.04352	1.18068	1.30707	1.42636
100	0.31054	0.37939	0.56167	0.80422	1.00048	1.16657	1.31511
200	0.56720	0.62564	0.70536	0.81306	0.94740	1.09716	1.25020
300	0.80810	0.86919	0.94273	1.03061	1.13306	1.24859	1.37373
400	1.03859	1.10313	1.17678	1.26018	1.35329	1.45571	1.56612
600	1.47803	1.54914	1.62636	1.70955	1.79840	1.89299	1.99261
800	1.89693	1.97379	2.0553	2.1410	2.2305	2.3241	2.4213
1,000	2.3007	2.3827	2.4684	2.5573	2.6486	2.7431	2.8406
1,200	2.6925	2.7791	2.8688	2.9608	3.0544	3.1507	3.2493
1,500	3.2624	3.3551	3.4501	3.5468	3.6440	3.7434	3.8443
2,000	4.1750	4.2762	4.3791	4.4828	4.5859	4.6905	4.7961
2,500	5.0518	5.1600	5.2699	5.3797	5.4881	5.5976	5.7077

† From A. Michels, S. R. DeGroot, and M. Geldermans, *Appl. Sci. Res.*, **A1**:55 (1947).

TABLE D-5. BIBLIOGRAPHY OF EXPERIMENTAL WORK ON pVT PROPERTIES OF PURE GASES

Gas	Pressure, atm		Temp. °C or as marked		Ref.†
	Min.	Max.	Min.	Max.	
Air.....	750	3,000		15	1
	1	3,000	0	200	2
	0	60		30	27
	0	105	0	200	41
Ammonia.....	97	4,490		30	54
	14.4	130.4	75	325	13
	968	11,600		30	23
Argon.....	100	1,100	0	210	50
	1,936	14,520		55	23
	13.9	60.7		116.62	31
	0	105	-100	400	41
Benzene.....	0	2,500	0	150	72
	18	3,000	0	150	81
	26	66	240	355	36
	14.68	358.53	150	300	17
<i>n</i> -Butane.....	0.68	680	100°F	460°F	81
	0	300	31.1°F	540°F	95
	1	204	70°F	250°F	123
	25.7	303.8	150	300	14
Isobutane.....	0.6	275	70°F	250°F	114
	25	250	150	250	15
	1	680	100°F	340°F	88
	1	50	0	500	60
Carbon dioxide.....	16	250	0	150	70
	75	3,000	0	150	71
	0	680	100°F	460°F	103
	0.1	1,000	70	200	8
Carbon monoxide.....	20	3,000	0	150	73
	141	223	37.2°K	41.2°K	40
Deuterium.....	9	3,000	0	150	69
	60	350	50	275	17a
Ethane.....	11	192.3	25	250	16
	0	680	100°F	460°F	102
	1	240	70°F	250°F	124
	11	200	150	325	10
Ethyl ether.....	20	3,000	0	150	66
Helium.....	2,906	14,520		65	23
	197	1,740	13.5	20.4	26
	0	140	0	50	27
	5.5	16.5	0	100	48
	9	292	0	150	82
	6	80	0	600	125
	100	1,000	-70	200	139

† See Bibliography in Appendix D.

TABLE D-5. BIBLIOGRAPHY OF EXPERIMENTAL WORK ON pVT PROPERTIES
OF PURE GASES (Continued)

Gas	Pressure, atm		Temp. °C or as marked		Ref.
	Min.	Max.	Min.	Max.	
<i>n</i> -Heptane	7	351	30	250	128
<i>n</i> -Hexane	0.1	10	100	275	49
	9.3	35.9	170	280	131
Hydrogen	1	1,000	0	400	6
	0	1,000	-70	20	7
	1,000	5,000	0	16	9
	1,940	12,600	30	65	23
	1	200	35°K	300°K	43
	100	1,000	0		61
	75	1,200	0	100	76
	10	3,000	0	150	68
	6	50	-244	-104	97
	25	1,000	0	300	138
	0	60	-212	100	140
	7	1,000	65.7°K	90.6°K	141
Hydrogen sulfide	0	681	40°F	340°F	104
Methane	0	1,000	-70	200	58
	25	380	0	150	74
	0	686	70°F	460°F	86
Methyl fluoride	0	150	0	150	77
Neon	0	150	-183	400	41
	20	90	-207.9		42
	32	494	0	100.8	67
	22	93	-217	20	89
Nitrogen	1	1,000	0	400	6
	0	1,000	-70	20	7
	1,000	5,000	0	16	9
	980	5,800	-175	200	19
	2,400	14,500		68	23
	28.5	54.7		-102	32
	100	1,000		0	61
	19	85	0	150	83
	200	3,000	0	150	84
	45	415	0	150	94
	25	1,000	0	300	138
Nitric oxide	30	160	-78.6	9	25
	0	170	40	220	35
Oxygen	1	3,000	0	200	2
	100	1,000		0	61
	5	125		24.95	64
	3	9	-152	-40	85
	22	66	0	20	90
	20	60	-117	-40	91
	35	66	0	20	132

TABLE D-5. BIBLIOGRAPHY OF EXPERIMENTAL WORK ON pVT PROPERTIES OF PURE GASES (*Continued*)

Gas	Pressure, atm		Temp. °C or as marked		Ref.
	Min.	Max.	Min.	Max.	
<i>n</i> -Pentane.....	0.7	205	70°F	220°F	121
	1	680	100°F	460°F	115
Isopentane.....	0	9,000	0	95	24
	5.6	312	100	225	49
Propane.....	23	305	96.8	275	12
	10	50	50	125	29
	1	140	30	336	30
	0	680	100°F	460°F	119
Propylene.....	10	215	30	250	62
	2	80	0	300	134
Water.....	1	50	100	550	28
	1	400	100	550	39
	4.7	218.2	150	374	52
	1	390	100	550	53
	24.2	344.6	30	374	129
Xenon.....	20.7	406.1	16.7	300	11

TABLE D-6. BIBLIOGRAPHY OF EXPERIMENTAL WORK ON pVT PROPERTIES OF BINARY GAS MIXTURES ABOVE 5 ATM

Gas mixtures	Max. pressure, atm	Temp., °C		Number of mixtures	Ref.†
		Min.	Max.		
Carbon dioxide, hydrogen.....	500	50	200	57
Carbon dioxide, hydrogen.....	500	50	200	63
Carbon dioxide, methane.....	680	40	240	4	100
Carbon dioxide, nitrogen.....	500	25	125	2	38
Carbon dioxide, nitrogen.....	500	0	200	57
Carbon dioxide, propane.....	680	5	240	4	108
Carbon monoxide, hydrogen.....	160	25	25	3	126
Carbon monoxide, hydrogen.....	1,000	0	300	55
Decane, methane.....	640	40	240	5	99
Ethane, methane.....	60	0	50	4	75
Ethane, methane.....	200	20	120	4	116
Ethane, methane.....	320	20	120	5	117
Ethane, nitrogen.....	680	5	240	3	111
Ethane, oxygen.....	1,000	0	300	55
Ethane, propane.....	680	-10	205	3	65
Ethane, propylene.....	220	100	250	4	61a
Ethylene, nitrogen.....	660	50	50	4	37
Ethylene, oxygen.....	125	25	75	3	64
Helium, hydrogen.....	125	25	175	11	33
Hexane, toluene.....	95	225	300	3	137
Ammonia, hydrogen.....	1,500	150	300	2	45
Ammonia, hydrogen.....	1,800	0	0	1	47
Ammonia, methane.....	1,675	150	300	46
Ammonia, nitrogen.....	1,500	150	300	1	45
Ammonia, nitrogen.....	60	0	0	7	59
Argon, ethylene.....	1,000	0	300	55
Argon, ethylene.....	125	25	25	5	64
Argon, helium.....	125	25	175	9	130
Argon, hydrogen.....	125	25	175	7	130
Argon, oxygen.....	125	25	25	1	64
Isobutane, methane.....	340	40	240	4	92
<i>n</i> -Butane, methane.....	350	100	300	3	18
<i>n</i> -Butane, methane.....	680	40	240	4	98
<i>n</i> -Butane, methane.....	240	70	250	9	113
<i>n</i> -Butane, methane.....	200	20	120	4	116
Isobutene, propene.....	680	40	280	4	34
Carbon dioxide, ethane.....	680	40	240	5	101
Hydrogen, methane.....	700	0	200	2	56
Hydrogen, nitrogen.....	1,000	0	0	8	4,5
Hydrogen, nitrogen.....	1,000	0	400	1	6
Hydrogen, nitrogen.....	1,000	-70	-20	1	7
Hydrogen, nitrogen.....	3,000	25	125	3	20
Hydrogen, nitrogen.....	1,000	0	200	"Several"	21

† See Bibliography in Appendix D.

TABLE D-6. BIBLIOGRAPHY OF EXPERIMENTAL WORK ON pVT PROPERTIES OF BINARY GAS MIXTURES ABOVE 5 ATM (*Continued*)

Gas mixtures	Max. pressure, atm	Temp., °C		Number of mixtures	Ref.
		Min.	Max.		
Hydrogen, nitrogen.....	1,000	0	300	55
Hydrogen, nitrogen.....	500	0	200	57
Hydrogen, nitrogen.....	500	50	200	63
Hydrogen, nitrogen.....	340	0	150	1	78
Hydrogen, nitrogen.....	1,000	-50	200	1	112
Hydrogen, nitrogen.....	680	5	240	1	122
Hydrogen, nitrogen.....	200	0	20	3	135
Hydrogen, nitrogen.....	1,000	0	300	4	138
Hydrogen sulfide, methane.....	680	5	170	5	106
Hydrogen sulfide, <i>n</i> -pentane.....	680	5	170	4	109
Methane, nitrogen.....	326	0	200	3	51
Methane, nitrogen.....	1,000	0	300	55
Methane, nitrogen.....	700	0	200	3	56
Methane, oxygen.....	1,000	0	300	55
Methane, isopentane.....	100	30	200	5	3
Methane, propane.....	680	5	240	4	105
Methane, propane.....	200	20	120	4	116
Methane, propane.....	200	20	90	8	120
Nitric oxide, nitrogen dioxide.....	475	5	170	15	127
Nitrogen, propane.....	410	125	150	6	136
Isopentane, propane.....	80	0	300	5	133
<i>n</i> -Pentane, propane.....	34	70	170	5	118
Propane, propene.....	680	-10	205	2	110

TABLE D-7. BIBLIOGRAPHY OF EXPERIMENTAL WORK ON pVT PROPERTIES OF MULTICOMPONENT GAS MIXTURES ABOVE 5 ATM

Gas mixture	Max. pressure, atm	Temp., °C		No. of mixtures	Ref.†
		Min.	Max.		
Air.....	1,000	0	300	55
Ammonia, hydrogen, nitrogen.....	1,500	150	300	2	45
Ammonia, hydrogen, nitrogen.....	300	0	150	3	79
Ammonia, hydrogen, nitrogen.....	300	75	150	1	80
Ammonia, hydrogen, nitrogen, argon, methane.....	300	75	150	1	80
<i>n</i> -Butane, decane, methane.....	680	40	240	10	107
Carbon dioxide, carbon monoxide, hydrogen, methane, nitrogen.....	680	5	240	1	122
Carbon dioxide, hydrogen, nitrogen.	500	0	200	57
Carbon dioxide, hydrogen, nitrogen.	500	50	200	63
Carbon dioxide, methane, misc. hydrocarbons.....	240	0	50	"Several"	96
Gasoline.....	36	150	360	1	44
Hydrogen, methane, nitrogen.....	800	-30	250	2	22
Hydrogen, methane, nitrogen.....	700	0	200	3	56
Illuminating gas.....	200	-50	50	1	93
Naphtha.....	36	150	360	1	44

† See Bibliography in Appendix D.

TABLE D-8. VAPOR HEAT CAPACITIES†
Values of C_p^* for Ideal-gas State in Btu/(lb mole)(°F)

Gas	-100°F	0°F	77°F	100°F	200°F	300°F	400°F	500°F	600°F
Water.....	7.96	7.99	8.02	8.03	8.12	8.22	8.34	8.49	8.64
Ammonia.....	7.68	8.15	8.52	8.58	9.01	9.44	9.85	10.25	10.62
Carbon dioxide...	7.80	8.39	8.86	9.00	9.55	10.08	10.50	10.89	11.22
Hydrogen sulfide...	7.80	8.00	8.14	8.18	8.36	8.55	8.73	8.92	9.10
Sulfur dioxide....	9.30	9.42	9.50	9.52	9.63	9.73	9.83	9.93	10.04
Methane.....	7.80	8.14	8.52	8.65	9.20	10.02	10.80	11.59	12.36
Ethylene.....	7.95	9.33	10.40	10.73	12.10	13.41	14.68	15.82	16.85
Ethane.....	9.70	11.32	12.56	21.93	14.64	16.30	17.98	19.55	21.04
Propane.....	13.30	15.40	17.55	18.20	20.90	23.55	26.05	28.32	30.43
n-Butane.....	17.80	21.10	23.60	24.40	27.76	31.05	34.25	37.20	39.85

† From W. C. Edminster and R. J. McGarry, *Chem. Eng. Progr.*, **45**:421 (1949).

TABLE D-9. THE COMPRESSION (k) AT 25°C OF VARIOUS MATERIALS†

$$k = - \frac{\Delta V}{V_0}$$

Pressure, bars	Water	Sodium chloride	Bessemer steel	Pyrex glass	Mercury	n-Butyl ether
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
500	0.0212	0.00205	0.00030	0.00151	0.00201	0.0439
1,000	0.0393	0.00409	0.00060	0.00303	0.00399	0.0747
1,500	0.0555	0.00611	0.00090	0.00456	0.00594	0.0964
2,000	0.0699	0.00812	0.00119	0.00608	0.00786	0.1156
3,000	0.0945	0.01208	0.00178	0.00915	0.01157	0.1441
4,000	0.1152	0.01598	0.00236	0.01224	0.01518	0.1665
5,000	0.1330	0.01982	0.00294	0.01534	0.01861	0.1843
6,000	0.1485	0.02360	0.00352	0.01846	0.02191	0.1998
7,000	0.1622	0.02731	0.00409	0.02159	0.02507	0.2132
8,000	0.1746	0.03095	0.00465	0.02475	0.02807	0.2246
9,000	0.1858	0.03454	0.00521	0.02792	0.03090	0.2353
10,000	0.1964	0.03806	0.00579	0.03111	0.03360	0.2448
11,000	(0.2059)	0.04151	0.00632	0.03432	0.03615	0.2532
12,000	(0.2147)	0.04492	0.00687	0.03754	0.03856	0.2608

† From D. M. Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressures," Oxford University Press, New York, 1940; data from Adams, *Am. J. Sci.*, **35**:1 (1938).

TABLE D-10. CRITICAL CONSTANTS OF ELEMENTS AND COMPOUNDS†

Name	Formula	t_c , °C	p_c , atm	ρ_c , g/cc
Ammonia.....	NH ₃	132.3	111.3	0.235
Argon.....	A	-122	48.0	0.531
Benzene.....	C ₆ H ₆	289	48.6	0.300
<i>n</i> -Butane.....	C ₄ H ₁₀	152.0	37.5	0.228
Isobutane.....	C ₄ H ₁₀	134.9	36.0	0.221
Carbon dioxide.....	CO ₂	31.0	72.9	0.468
Carbon monoxide.....	CO	-140	34.5	0.301
Chlorine.....	Cl ₂	144	76.1	0.573
Ethane.....	C ₂ H ₆	32.3	48.2	0.203
Ethyl alcohol.....	C ₂ H ₅ OH	243	63.0	0.276
Ethylene.....	C ₂ H ₄	9.90	50.5	0.227
Helium.....	He	-267.9	2.26	0.0693
<i>n</i> -Heptane.....	C ₇ H ₁₆	267.0	27.0	0.235
<i>n</i> -Hexane.....	C ₆ H ₁₄	234.7	29.9	0.234
Hydrazine.....	N ₂ H ₄	380	145	
Hydrogen.....	H ₂	-239.9	12.80	0.0310
Hydrogen sulfide.....	H ₂ S	100.4	88.9	0.349
Mercury.....	Hg	>1550	>200	4-5
Methane.....	CH ₄	-82.1	45.8	0.162
Methyl alcohol.....	CH ₃ OH	240.0	78.5	0.272
Neon.....	Ne	-228.7	26.9	0.484
Nitrogen.....	N ₂	-147.0	33.5	0.311
<i>n</i> -Octane.....	C ₈ H ₁₈	296.2	24.6	0.233
Oxygen.....	O ₂	-118.4	50.1	0.41
<i>n</i> -Pentane.....	C ₅ H ₁₂	196.6	33.3	0.232
Isopentane (2-methylbutane).....	C ₅ H ₁₂	187.8	32.9	0.234
Neopentane (2,2 dimethylpropane)....	C ₅ H ₁₂	160.6	31.6	0.238
Propane.....	C ₃ H ₈	96.8	42.0	0.220
Propene.....	C ₃ H ₆	91.8	45.6	0.233
Sulfur dioxide.....	SO ₂	157.5	77.8	0.524
Water.....	H ₂ O	374.2	218.3	0.32

† Selected values from K. A. Kobe and R. E. Lynn, Jr., *Chem. Rev.*, **52**:117-136 (1953).

TABLE D-11. BIBLIOGRAPHY OF PROPERTIES OF LIQUIDS AND SOLIDS

Property	Ref.
Linear thermal expansion of the solid elements.....	a
Linear thermal expansion of miscellaneous substances.....	b
Cubical thermal expansion of liquids.....	c
Cubical thermal expansion of solids.....	d
Compressibilities of liquids.....	e
(a) J. H. Perry, editor, "Chemical Engineers' Handbook," 3rd ed., p. 200, McGraw-Hill Book Company, Inc., New York, 1950. (b) <i>ibid.</i> , p. 201; (c) <i>ibid.</i> , p. 202; (d) <i>ibid.</i> , p. 202; (e) <i>ibid.</i> , p. 209.	

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS†
(Values above horizontal lines are for liquids; below, for gases)
† Prepared by A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, *Univ. of Wise. Eng. Expt. Sta. Rept.* 4, October, 1955.

pR	0.01				0.10				0.20			
	W	I		III	W	I		III	W	I		III
		II	III			II	III			II	III	
z	0.23	0.25	0.27	0.29	0.23	0.25	0.27	0.29	0.23	0.25	0.27	0.29
T_R	0.758	0.758	0.743	0.714	0.819	0.817	0.805	0.781
Sat. gas	0.866	0.895	0.898	0.900	0.820	0.830	0.833	0.839
Sat. liq.	0.0116	0.014	0.015	0.018	0.0227	0.028	0.030	0.034
T_R												
0.50	0.0015	0.985	0.986	0.988	0.0150	0.017	0.018	0.021	0.0299	0.032	0.037	0.042
0.60	0.0013	0.987	0.988	0.990	0.0130	0.0145	0.016	0.019	0.0260	0.028	0.033	0.038
0.70	0.988	0.989	0.990	0.993	0.0119	0.0140	0.015	0.018	0.0238	0.027	0.030	0.035
0.80	0.993	0.991	0.992	0.994	0.0114	0.912	0.921	0.925	0.0228	0.026	0.030	0.034
0.90	0.997	0.993	0.994	0.995	0.949	0.940	0.947	0.950	0.886	0.884	0.890	0.900
0.92	0.997	0.994	0.994	0.995	0.954	0.945	0.951	0.955	0.897	0.888	0.901	0.910
0.94	0.998	0.994	0.994	0.995	0.958	0.950	0.955	0.959	0.907	0.907	0.909	0.916
0.96	0.998	0.994	0.995	0.995	0.962	0.954	0.958	0.963	0.915	0.913	0.915	0.923
0.98	0.998	0.994	0.995	0.996	0.964	0.959	0.962	0.965	0.922	0.918	0.922	0.929
1.00	0.998	0.995	0.995	0.996	0.967	0.963	0.965	0.969	0.928	0.923	0.927	0.934
1.01	0.999	0.995	0.996	0.996	0.968	0.964	0.966	0.970	0.931	0.925	0.930	0.937
1.02	0.999	0.995	0.996	0.996	0.970	0.965	0.967	0.971	0.934	0.929	0.933	0.939
1.03	0.999	0.995	0.996	0.996	0.971	0.967	0.968	0.972	0.936	0.931	0.935	0.941
1.04	0.999	0.995	0.996	0.996	0.972	0.969	0.970	0.973	0.939	0.934	0.938	0.943
1.05	0.999	0.996	0.996	0.997	0.973	0.971	0.971	0.974	0.940	0.936	0.940	0.946
1.06	0.999	0.996	0.996	0.997	0.974	0.972	0.972	0.975	0.942	0.939	0.942	0.948
1.07	0.999	0.996	0.996	0.997	0.975	0.973	0.973	0.976	0.945	0.941	0.944	0.950
1.08	0.999	0.996	0.996	0.997	0.976	0.974	0.974	0.977	0.946	0.943	0.946	0.952
1.09	0.999	0.996	0.997	0.997	0.977	0.975	0.975	0.978	0.949	0.945	0.948	0.954
1.10	0.999	0.996	0.997	0.998	0.978	0.976	0.976	0.979	0.951	0.948	0.950	0.955
1.12	0.999	0.997	0.997	0.998	0.979	0.977	0.977	0.980	0.954	0.951	0.953	0.957
1.14	0.999	0.997	0.997	0.998	0.980	0.979	0.979	0.981	0.958	0.953	0.957	0.959
1.16	1.000	0.997	0.997	0.998	0.982	0.981	0.980	0.982	0.960	0.957	0.960	0.962
1.18	1.000	0.997	0.997	0.998	0.983	0.982	0.982	0.983	0.963	0.960	0.963	0.964
1.20	1.000	0.997	0.998	0.998	0.984	0.983	0.983	0.984	0.965	0.963	0.965	0.967
1.30	1.000	0.998	0.998	0.998	0.989	0.987	0.987	0.988	0.974	0.970	0.974	0.975
1.40	1.000	0.998	0.998	0.999	0.992	0.989	0.990	0.991	0.981	0.980	0.982	0.982
1.50	1.001	0.998	0.999	0.999	0.992	0.991	0.991	0.992	0.986	0.985	0.986	0.986
1.60	1.001	0.998	0.999	1.000	0.997	0.992	0.992	0.992	0.990	0.988	0.988	0.988
1.70	1.001	0.998	0.999	1.000	0.998	0.992	0.992	0.992	0.992	0.989	0.989	0.989
1.80	0.999	0.999	1.000	0.993	0.993	0.993	0.991	0.991	0.991
1.90	0.999	1.000	1.000	0.993	0.993	0.993	0.993	0.993	0.993
2.00	0.999	1.000	1.000	0.994	0.994	0.994	0.994	0.994	0.994
3.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
6.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
8.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
15.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE D-12. COMPRESSIBILITY FACTORS 2 OF PURE GASES AND LIQUIDS (Continued)

P, K	0.30						0.40						0.50					
	W		II		III		W		II		III		W		II		III	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
z	0.23	0.27	0.25	0.27	0.29	0.26	0.23	0.27	0.25	0.27	0.29	0.26	0.23	0.27	0.25	0.27	0.29	0.26
T_R	0.858	0.846	0.856	0.846	0.826	0.826	0.889	0.876	0.885	0.876	0.861	0.861	0.914	0.900	0.910	0.900	0.892	0.892
Sat. gas	0.760	0.783	0.780	0.783	0.760	0.783	0.700	0.738	0.732	0.738	0.746	0.746	0.650	0.681	0.650	0.681	0.698	0.698
Sat. liq.	0.0347	0.045	0.040	0.045	0.051	0.051	0.047	0.052	0.052	0.060	0.068	0.068	0.060	0.077	0.069	0.077	0.086	0.086
T_R	0.0438	0.055	0.048	0.055	0.063	0.063	0.0597	0.073	0.062	0.073	0.084	0.084	0.0745	0.093	0.080	0.093	0.105	0.105
0.50	0.0359	0.049	0.043	0.049	0.056	0.056	0.0519	0.065	0.057	0.065	0.075	0.075	0.0648	0.071	0.071	0.071	0.094	0.094
0.60	0.0356	0.046	0.040	0.046	0.052	0.052	0.0474	0.061	0.053	0.061	0.070	0.070	0.0391	0.066	0.066	0.066	0.087	0.087
0.70	0.0342	0.044	0.039	0.044	0.051	0.051	0.0456	0.059	0.051	0.059	0.067	0.067	0.0308	0.064	0.064	0.064	0.084	0.084
0.80	0.813	0.826	0.822	0.826	0.840	0.840	0.721	0.764	0.745	0.764	0.775	0.775	0.6590	0.077	0.068	0.077	0.705	0.705
0.90	0.836	0.842	0.835	0.842	0.852	0.852	0.756	0.783	0.767	0.783	0.789	0.789	0.662	0.710	0.692	0.710	0.729	0.729
0.92	0.851	0.856	0.853	0.856	0.862	0.862	0.786	0.798	0.790	0.798	0.806	0.806	0.712	0.735	0.721	0.735	0.752	0.752
0.94	0.865	0.868	0.864	0.868	0.876	0.876	0.809	0.817	0.805	0.817	0.820	0.820	0.746	0.761	0.750	0.761	0.773	0.773
0.96	0.877	0.879	0.873	0.879	0.885	0.885	0.826	0.832	0.824	0.832	0.832	0.832	0.774	0.782	0.772	0.782	0.793	0.793
0.98	0.888	0.889	0.882	0.889	0.893	0.893	0.844	0.846	0.838	0.846	0.852	0.852	0.798	0.801	0.792	0.801	0.808	0.808
1.00	0.893	0.893	0.886	0.893	0.897	0.897	0.851	0.852	0.844	0.852	0.858	0.858	0.805	0.809	0.800	0.809	0.816	0.816
1.01	0.898	0.897	0.890	0.897	0.902	0.902	0.858	0.858	0.852	0.858	0.864	0.864	0.817	0.817	0.808	0.817	0.824	0.824
1.02	0.901	0.901	0.894	0.901	0.906	0.906	0.863	0.863	0.856	0.863	0.869	0.869	0.824	0.825	0.818	0.825	0.831	0.831
1.03	0.906	0.905	0.898	0.905	0.910	0.910	0.870	0.868	0.861	0.868	0.874	0.874	0.834	0.834	0.824	0.834	0.838	0.838
1.04	0.910	0.908	0.902	0.908	0.913	0.913	0.875	0.873	0.868	0.873	0.879	0.879	0.842	0.838	0.833	0.838	0.845	0.845
1.05	0.912	0.911	0.906	0.911	0.918	0.918	0.880	0.878	0.873	0.878	0.886	0.886	0.848	0.848	0.840	0.848	0.852	0.852
1.06	0.916	0.916	0.910	0.916	0.920	0.920	0.885	0.883	0.878	0.883	0.889	0.889	0.855	0.855	0.846	0.855	0.857	0.857
1.07	0.920	0.918	0.913	0.918	0.923	0.923	0.890	0.886	0.882	0.886	0.891	0.891	0.861	0.861	0.851	0.861	0.866	0.866
1.08	0.922	0.920	0.918	0.920	0.926	0.926	0.893	0.890	0.886	0.890	0.893	0.893	0.866	0.862	0.855	0.862	0.865	0.865
1.09	0.925	0.923	0.919	0.923	0.927	0.927	0.898	0.894	0.889	0.894	0.899	0.899	0.872	0.866	0.860	0.872	0.870	0.870
1.10	0.930	0.928	0.924	0.928	0.931	0.931	0.905	0.901	0.896	0.901	0.904	0.904	0.882	0.876	0.870	0.882	0.878	0.878
1.12	0.934	0.933	0.928	0.933	0.936	0.936	0.913	0.907	0.903	0.907	0.912	0.912	0.890	0.884	0.878	0.887	0.887	0.887
1.14	0.940	0.937	0.934	0.937	0.939	0.939	0.918	0.913	0.911	0.913	0.917	0.917	0.896	0.891	0.886	0.894	0.894	0.894
1.16	0.943	0.942	0.937	0.942	0.943	0.943	0.923	0.918	0.915	0.918	0.923	0.923	0.905	0.903	0.898	0.903	0.903	0.903
1.18	0.946	0.946	0.942	0.946	0.948	0.948	0.928	0.924	0.920	0.924	0.929	0.929	0.911	0.905	0.901	0.911	0.916	0.916
1.20	0.961	0.961	0.959	0.961	0.963	0.963	0.948	0.945	0.944	0.945	0.946	0.946	0.937	0.931	0.931	0.937	0.932	0.932
1.30	0.968	0.970	0.970	0.972	0.973	0.973	0.960	0.957	0.957	0.959	0.961	0.961	0.954	0.948	0.948	0.954	0.950	0.950
1.40	0.974	0.980	0.980	0.980	0.980	0.980	0.971	0.968	0.968	0.970	0.973	0.973	0.966	0.963	0.961	0.966	0.965	0.965
1.50	0.984	0.985	0.984	0.985	0.985	0.985	0.979	0.978	0.978	0.978	0.978	0.978	0.975	0.970	0.970	0.975	0.970	0.970
1.60	0.988	0.989	0.988	0.989	0.989	0.989	0.984	0.984	0.984	0.984	0.984	0.984	0.981	0.980	0.978	0.981	0.980	0.980
1.70	0.991	0.991	0.991	0.991	0.991	0.991	0.987	0.987	0.987	0.987	0.987	0.987	0.985	0.985	0.985	0.985	0.985	0.985
1.80	0.993	0.993	0.993	0.993	0.993	0.993	0.991	0.991	0.991	0.991	0.991	0.991	0.989	0.989	0.989	0.989	0.989	0.989
1.90	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994
2.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
3.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
6.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
8.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
15.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

pr.	0.60						0.70						0.80					
	I		II		III		I		II		III		I		II		III	
	W		W		W		W		W		W		W		W		W	
z_c	0.23				0.29		0.23		0.27		0.29		0.23		0.27		0.29	
T_R	0.936	0.932	0.928	0.919	0.919	0.919	0.954	0.952	0.949	0.949	0.942	0.942	0.971	0.969	0.967	0.967	0.963	0.963
Sat. gas	0.062	0.628	0.641	0.650	0.650	0.650	0.548	0.570	0.583	0.583	0.596	0.596	0.486	0.505	0.519	0.519	0.536	0.536
Sat. liq.	0.0749	0.086	0.096	0.103	0.103	0.103	0.091	0.103	0.114	0.114	0.125	0.125	0.110	0.124	0.136	0.136	0.150	0.150
T_R																		
0.50	0.0894	0.096	0.110	0.126	0.126	0.126	0.104	0.112	0.128	0.128	0.147	0.147	0.119	0.128	0.147	0.147	0.168	0.168
0.60	0.0776	0.086	0.098	0.112	0.112	0.112	0.0904	0.100	0.113	0.113	0.131	0.131	0.103	0.114	0.130	0.130	0.149	0.149
0.70	0.0709	0.079	0.092	0.104	0.104	0.104	0.0826	0.092	0.106	0.106	0.121	0.121	0.0942	0.105	0.121	0.121	0.138	0.138
0.80	0.0679	0.077	0.088	0.101	0.101	0.101	0.0790	0.089	0.102	0.102	0.117	0.117	0.0900	0.102	0.116	0.116	0.133	0.133
0.90	0.0706	0.080	0.091	0.103	0.103	0.103	0.0187	0.092	0.105	0.105	0.120	0.120	0.0927	0.105	0.120	0.120	0.136	0.136
0.92	0.0721	0.082	0.093	0.652	0.652	0.652	0.0834	0.095	0.108	0.108	0.123	0.123	0.0946	0.107	0.122	0.122	0.139	0.139
0.94	0.0748	0.085	0.096	0.684	0.684	0.684	0.0866	0.098	0.111	0.111	0.126	0.126	0.0961	0.111	0.126	0.126	0.143	0.143
0.96	0.638	0.684	0.700	0.708	0.708	0.708	0.0933	0.598	0.613	0.613	0.630	0.630	0.105	0.117	0.133	0.133	0.150	0.150
0.98	0.675	0.712	0.731	0.736	0.736	0.736	0.632	0.636	0.665	0.665	0.669	0.669	0.528	0.555	0.580	0.580	0.598	0.598
1.00	0.709	0.744	0.755	0.760	0.760	0.760	0.680	0.690	0.704	0.704	0.710	0.710	0.605	0.616	0.640	0.640	0.652	0.652
1.01	0.728	0.756	0.766	0.772	0.772	0.772	0.700	0.706	0.718	0.718	0.726	0.726	0.634	0.642	0.661	0.661	0.671	0.671
1.02	0.744	0.765	0.776	0.782	0.782	0.782	0.718	0.720	0.732	0.732	0.738	0.738	0.659	0.664	0.679	0.679	0.689	0.689
1.03	0.754	0.778	0.785	0.792	0.792	0.792	0.732	0.735	0.745	0.745	0.751	0.751	0.679	0.682	0.696	0.696	0.701	0.701
1.04	0.767	0.786	0.794	0.800	0.800	0.800	0.746	0.745	0.756	0.756	0.760	0.760	0.697	0.699	0.709	0.709	0.715	0.715
1.05	0.777	0.798	0.802	0.808	0.808	0.808	0.760	0.758	0.766	0.766	0.770	0.770	0.715	0.716	0.723	0.723	0.727	0.727
1.06	0.785	0.805	0.809	0.818	0.818	0.818	0.771	0.769	0.775	0.775	0.780	0.780	0.728	0.728	0.734	0.734	0.739	0.739
1.07	0.795	0.811	0.817	0.824	0.824	0.824	0.782	0.776	0.782	0.782	0.788	0.788	0.743	0.743	0.750	0.750	0.750	0.750
1.08	0.805	0.818	0.824	0.829	0.829	0.829	0.793	0.786	0.793	0.793	0.797	0.797	0.756	0.756	0.762	0.762	0.762	0.762
1.09	0.813	0.823	0.830	0.834	0.834	0.834	0.801	0.792	0.798	0.798	0.802	0.802	0.766	0.766	0.773	0.773	0.773	0.773
1.10	0.822	0.831	0.837	0.840	0.840	0.840	0.810	0.800	0.805	0.805	0.808	0.808	0.779	0.779	0.785	0.785	0.785	0.785
1.12	0.840	0.842	0.849	0.852	0.852	0.852	0.826	0.814	0.818	0.818	0.822	0.822	0.800	0.800	0.804	0.804	0.804	0.804
1.14	0.855	0.852	0.859	0.863	0.863	0.863	0.839	0.827	0.830	0.830	0.832	0.832	0.815	0.815	0.819	0.819	0.819	0.819
1.16	0.868	0.861	0.870	0.874	0.874	0.874	0.850	0.840	0.842	0.842	0.844	0.844	0.827	0.827	0.831	0.831	0.831	0.831
1.18	0.878	0.870	0.878	0.880	0.880	0.880	0.862	0.848	0.852	0.852	0.856	0.856	0.838	0.838	0.842	0.842	0.842	0.842
1.20	0.889	0.880	0.888	0.888	0.888	0.888	0.871	0.860	0.862	0.862	0.864	0.864	0.848	0.848	0.852	0.852	0.852	0.852
1.30	0.921	0.916	0.916	0.918	0.918	0.918	0.909	0.900	0.900	0.900	0.902	0.902	0.890	0.886	0.888	0.888	0.888	0.888
1.40	0.940	0.934	0.937	0.940	0.940	0.940	0.932	0.926	0.928	0.928	0.930	0.930	0.922	0.920	0.922	0.922	0.922	0.922
1.50	0.954	0.950	0.953	0.956	0.956	0.956	0.949	0.947	0.948	0.948	0.949	0.949	0.941	0.940	0.945	0.945	0.945	0.945
1.60	0.965	0.965	0.965	0.970	0.970	0.970	0.963	0.963	0.964	0.964	0.965	0.965	0.958	0.958	0.960	0.960	0.960	0.960
1.70	0.973	0.971	0.974	0.977	0.977	0.977	0.972	0.974	0.974	0.974	0.975	0.975	0.968	0.970	0.972	0.972	0.972	0.972
1.80	0.982	0.982	0.982	0.982	0.982	0.982	0.982	0.982	0.982	0.982	0.980	0.980	0.980	0.980	0.980
1.90	0.987	0.987	0.987	0.987	0.987	0.987	0.987	0.987	0.987	0.987	0.981	0.981	0.981	0.981	0.981
2.00	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.990	0.990	0.990	0.990	0.990
3.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
6.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
8.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
15.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

PR.	0.9						1.0						1.05					
	I		II		III		I		II		III		I		II		III	
	W	I	II	III	W	I	II	I	II	III	W	I	II	I	II	III	W	I
$z_{0.001}$	0.23	0.25	0.27	0.29	0.23	0.25	0.27	0.25	0.27	0.29	0.23	0.25	0.27	0.25	0.27	0.29	0.23	0.27
T_{Ra}	0.986	0.985	0.984	0.982	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Sat. gas	0.415	0.427	0.443	0.460	0.232	0.250	0.270	0.232	0.250	0.270	0.232	0.250	0.270	0.232	0.250	0.270	0.232	0.250
Sat. liquid	0.136	0.152	0.164	0.177	0.232	0.250	0.270	0.232	0.250	0.270	0.232	0.250	0.270	0.232	0.250	0.270	0.232	0.250
T_R																		
0.50	0.134	0.144	0.165	0.189	0.148	0.160	0.183	0.160	0.183	0.210	0.156	0.168	0.156	0.168	0.192	0.220	0.156	0.220
0.60	0.116	0.128	0.147	0.168	0.129	0.142	0.163	0.129	0.163	0.186	0.136	0.149	0.136	0.149	0.171	0.196	0.136	0.196
0.70	0.106	0.118	0.136	0.155	0.117	0.130	0.151	0.117	0.151	0.171	0.106	0.123	0.106	0.123	0.145	0.168	0.106	0.168
0.80	0.101	0.111	0.131	0.150	0.112	0.126	0.145	0.112	0.145	0.169	0.101	0.117	0.101	0.117	0.136	0.155	0.101	0.155
0.90	0.104	0.117	0.134	0.153	0.122	0.139	0.158	0.122	0.158	0.170	0.104	0.120	0.104	0.120	0.136	0.155	0.104	0.155
0.92	0.105	0.120	0.137	0.155	0.116	0.133	0.151	0.116	0.151	0.170	0.105	0.121	0.105	0.121	0.139	0.158	0.105	0.158
0.94	0.109	0.124	0.141	0.159	0.120	0.136	0.155	0.120	0.155	0.173	0.109	0.125	0.109	0.125	0.143	0.162	0.109	0.162
0.96	0.115	0.130	0.147	0.166	0.126	0.143	0.161	0.126	0.161	0.182	0.115	0.132	0.115	0.132	0.149	0.169	0.115	0.169
0.98	0.127	0.143	0.161	0.180	0.136	0.157	0.174	0.136	0.174	0.195	0.127	0.140	0.127	0.140	0.161	0.181	0.127	0.181
1.00	0.515	0.500	0.520	0.544	0.232	0.250	0.270	0.232	0.270	0.290	0.194	0.218	0.194	0.218	0.230	0.237	0.194	0.230
1.01	0.556	0.550	0.568	0.580	0.442	0.360	0.424	0.442	0.424	0.464	0.343	0.272	0.343	0.272	0.365	0.380	0.343	0.365
1.02	0.591	0.592	0.602	0.619	0.508	0.484	0.509	0.508	0.509	0.522	0.454	0.410	0.454	0.410	0.463	0.466	0.454	0.463
1.03	0.618	0.620	0.627	0.640	0.547	0.538	0.555	0.547	0.555	0.564	0.505	0.486	0.505	0.486	0.505	0.518	0.505	0.505
1.04	0.643	0.646	0.650	0.662	0.581	0.577	0.585	0.581	0.585	0.596	0.546	0.537	0.546	0.537	0.546	0.558	0.546	0.558
1.05	0.665	0.664	0.670	0.678	0.610	0.600	0.611	0.610	0.611	0.620	0.581	0.566	0.581	0.566	0.577	0.587	0.581	0.577
1.06	0.683	0.683	0.687	0.694	0.632	0.625	0.633	0.632	0.633	0.639	0.607	0.595	0.607	0.595	0.603	0.609	0.607	0.603
1.07	0.701	0.696	0.703	0.708	0.655	0.646	0.654	0.655	0.654	0.658	0.631	0.620	0.631	0.620	0.627	0.630	0.631	0.627
1.08	0.713	0.710	0.715	0.723	0.675	0.665	0.671	0.675	0.671	0.676	0.653	0.639	0.653	0.639	0.647	0.653	0.653	0.647
1.09	0.729	0.721	0.726	0.730	0.691	0.680	0.686	0.691	0.686	0.689	0.670	0.657	0.670	0.657	0.662	0.668	0.670	0.662
1.10	0.743	0.731	0.738	0.742	0.707	0.694	0.700	0.707	0.700	0.702	0.689	0.675	0.689	0.675	0.678	0.682	0.689	0.678
1.12	0.765	0.753	0.756	0.760	0.734	0.718	0.723	0.734	0.723	0.726	0.718	0.702	0.718	0.702	0.704	0.708	0.718	0.704
1.14	0.785	0.772	0.773	0.777	0.756	0.740	0.745	0.756	0.745	0.748	0.742	0.724	0.742	0.724	0.731	0.735	0.742	0.731
1.16	0.803	0.786	0.790	0.793	0.780	0.758	0.764	0.780	0.764	0.766	0.765	0.746	0.765	0.746	0.750	0.752	0.765	0.750
1.18	0.817	0.801	0.805	0.808	0.795	0.776	0.780	0.795	0.780	0.782	0.783	0.765	0.783	0.765	0.772	0.778	0.783	0.772
1.20	0.831	0.817	0.818	0.822	0.810	0.792	0.795	0.810	0.795	0.799	0.799	0.780	0.799	0.780	0.787	0.788	0.799	0.787
1.30	0.883	0.872	0.874	0.876	0.866	0.855	0.857	0.866	0.857	0.860	0.860	0.848	0.860	0.848	0.849	0.851	0.860	0.849
1.40	0.912	0.910	0.912	0.914	0.902	0.897	0.899	0.902	0.899	0.900	0.897	0.892	0.897	0.892	0.892	0.894	0.897	0.892
1.50	0.934	0.937	0.938	0.939	0.926	0.926	0.929	0.926	0.929	0.930	0.926	0.926	0.926	0.926	0.922	0.925	0.926	0.922
1.60	0.952	0.955	0.955	0.956	0.946	0.948	0.948	0.946	0.948	0.952	0.946	0.948	0.946	0.948	0.943	0.948	0.946	0.943
1.70	0.963	0.967	0.968	0.968	0.959	0.963	0.964	0.959	0.964	0.965	0.965	0.963	0.965	0.963	0.958	0.962	0.965	0.958
1.80	0.977	0.977	0.978	0.978	0.978	0.970	0.974	0.978	0.974	0.974	0.974	0.970	0.974	0.970	0.970	0.972	0.974	0.970
1.90	0.985	0.985	0.985	0.985	0.985	0.983	0.983	0.985	0.983	0.983	0.983	0.983	0.983	0.983	0.983	0.983	0.983	0.983
2.00	0.990	0.990	0.990	0.990	0.990	0.988	0.988	0.988	0.988	0.988	0.988	0.988	0.988	0.988	0.986	0.987	0.988	0.986
3.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
6.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
8.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
15.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

PR	1.10				1.15				1.20			
	W	I	II	III	W	I	II	III	W	I	II	III
z	0.23	0.25	0.27	0.29	0.23	0.25	0.27	0.29	0.23	0.25	0.27	0.29
T_R												
0.50	0.163	0.176	0.201	0.231	0.170	0.184	0.211	0.241	0.178	0.184	0.211	0.241
0.60	0.142	0.156	0.179	0.205	0.148	0.163	0.187	0.214	0.154	0.163	0.187	0.214
0.70	0.129	0.144	0.165	0.190	0.135	0.151	0.173	0.198	0.140	0.150	0.173	0.198
0.80	0.123	0.139	0.159	0.182	0.128	0.145	0.166	0.190	0.134	0.145	0.166	0.190
0.90	0.125	0.142	0.162	0.185	0.130	0.148	0.169	0.193	0.135	0.148	0.169	0.193
0.92	0.127	0.145	0.165	0.187	0.132	0.151	0.172	0.195	0.137	0.151	0.172	0.195
0.94	0.130	0.149	0.169	0.191	0.136	0.155	0.176	0.199	0.141	0.155	0.176	0.199
0.96	0.136	0.155	0.176	0.198	0.142	0.161	0.183	0.206	0.146	0.161	0.183	0.206
0.98	0.145	0.168	0.189	0.212	0.150	0.174	0.195	0.210	0.153	0.174	0.195	0.210
1.00	0.163	0.214	0.224	0.228	0.166	0.215	0.223	0.223	0.164	0.215	0.223	0.223
1.01	0.214	0.245	0.256	0.290	0.191	0.239	0.246	0.232	0.183	0.239	0.246	0.232
1.02	0.381	0.353	0.360	0.398	0.282	0.314	0.316	0.325	0.227	0.325	0.316	0.325
1.03	0.458	0.430	0.461	0.470	0.400	0.395	0.408	0.415	0.329	0.395	0.408	0.415
1.04	0.511	0.498	0.505	0.510	0.466	0.459	0.471	0.475	0.419	0.459	0.471	0.475
1.05	0.549	0.536	0.541	0.551	0.510	0.505	0.513	0.520	0.479	0.505	0.513	0.520
1.06	0.578	0.560	0.568	0.578	0.546	0.540	0.545	0.545	0.515	0.540	0.545	0.545
1.07	0.606	0.590	0.594	0.603	0.580	0.570	0.573	0.574	0.551	0.570	0.573	0.574
1.08	0.631	0.611	0.616	0.628	0.607	0.593	0.597	0.600	0.581	0.593	0.597	0.600
1.09	0.650	0.635	0.637	0.644	0.628	0.615	0.618	0.620	0.605	0.615	0.618	0.620
1.10	0.670	0.654	0.655	0.660	0.653	0.636	0.639	0.641	0.629	0.636	0.639	0.641
1.12	0.701	0.685	0.686	0.690	0.684	0.668	0.672	0.674	0.666	0.668	0.672	0.674
1.14	0.728	0.709	0.712	0.716	0.713	0.694	0.698	0.700	0.698	0.698	0.698	0.700
1.16	0.752	0.732	0.735	0.738	0.739	0.720	0.724	0.726	0.725	0.725	0.724	0.726
1.18	0.771	0.753	0.756	0.757	0.759	0.742	0.745	0.748	0.747	0.742	0.745	0.748
1.20	0.789	0.772	0.773	0.774	0.778	0.761	0.763	0.765	0.767	0.761	0.763	0.765
1.20	0.853	0.841	0.841	0.843	0.846	0.834	0.835	0.837	0.838	0.834	0.835	0.837
1.40	0.863	0.886	0.888	0.888	0.885	0.880	0.882	0.884	0.881	0.880	0.882	0.884
1.50	0.919	0.915	0.918	0.921	0.915	0.912	0.914	0.916	0.911	0.912	0.914	0.916
1.60	0.941	0.934	0.940	0.944	0.938	0.938	0.938	0.940	0.935	0.938	0.938	0.935
1.70	0.955	0.936	0.956	0.958	0.953	0.934	0.954	0.955	0.951	0.934	0.954	0.955
1.80	0.968	0.968	0.968	0.969	0.966	0.965	0.966	0.966	0.966	0.965	0.966	0.966
1.90	0.976	0.976	0.977	0.978	0.973	0.973	0.974	0.976	0.974	0.973	0.974	0.976
2.00	0.984	0.984	0.984	0.986	0.982	0.982	0.982	0.985	0.981	0.982	0.982	0.985
3.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
6.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
8.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
15.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

T_R	1.25			1.30			1.35			1.40			1.45		
	W	II	W'	II	W'	II	W	II	W'	II	W'	II	W	II	W'
	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23
0.50	0.185	0.229	0.192	0.238	0.200	0.247	0.207	0.256	0.207	0.256	0.214	0.265	0.214	0.265	0.214
0.60	0.160	0.203	0.167	0.211	0.173	0.219	0.180	0.227	0.180	0.227	0.186	0.235	0.186	0.235	0.186
0.70	0.146	0.188	0.152	0.195	0.158	0.202	0.163	0.210	0.163	0.210	0.169	0.217	0.169	0.217	0.169
0.80	0.139	0.180	0.144	0.187	0.150	0.194	0.155	0.201	0.155	0.201	0.161	0.208	0.161	0.208	0.161
0.90	0.141	0.183	0.146	0.190	0.151	0.197	0.156	0.203	0.156	0.203	0.162	0.210	0.162	0.210	0.162
0.92	0.143	0.185	0.148	0.192	0.153	0.199	0.158	0.206	0.158	0.206	0.163	0.213	0.163	0.213	0.163
0.94	0.147	0.190	0.152	0.197	0.156	0.203	0.161	0.210	0.161	0.210	0.166	0.217	0.166	0.217	0.166
0.96	0.151	0.196	0.156	0.203	0.162	0.210	0.166	0.217	0.166	0.217	0.172	0.223	0.172	0.223	0.172
0.98	0.159	0.209	0.164	0.216	0.169	0.222	0.174	0.228	0.174	0.228	0.179	0.235	0.179	0.235	0.179
1.00	0.171	0.223	0.174	0.225	0.178	0.230	0.182	0.234	0.182	0.234	0.187	0.241	0.187	0.241	0.187
1.01	0.183	0.242	0.185	0.242	0.188	0.246	0.190	0.246	0.190	0.246	0.195	0.259	0.195	0.259	0.195
1.02	0.209	0.282	0.207	0.271	0.206	0.267	0.202	0.264	0.202	0.264	0.205	0.270	0.205	0.270	0.205
1.03	0.268	0.343	0.254	0.336	0.238	0.302	0.220	0.288	0.220	0.288	0.221	0.292	0.221	0.292	0.221
1.04	0.368	0.396	0.333	0.364	0.298	0.345	0.254	0.323	0.254	0.323	0.251	0.316	0.251	0.316	0.251
1.05	0.438	0.444	0.400	0.415	0.359	0.389	0.311	0.366	0.311	0.366	0.299	0.346	0.299	0.346	0.299
1.06	0.485	0.488	0.450	0.455	0.414	0.430	0.370	0.403	0.370	0.403	0.351	0.380	0.351	0.380	0.351
1.07	0.525	0.529	0.496	0.493	0.465	0.467	0.427	0.438	0.427	0.438	0.405	0.415	0.405	0.415	0.405
1.08	0.559	0.552	0.534	0.522	0.507	0.500	0.474	0.472	0.474	0.472	0.452	0.447	0.452	0.447	0.452
1.09	0.590	0.579	0.562	0.550	0.538	0.531	0.507	0.507	0.507	0.507	0.488	0.481	0.488	0.481	0.488
1.10	0.611	0.599	0.591	0.574	0.569	0.553	0.541	0.534	0.541	0.534	0.524	0.512	0.524	0.512	0.524
1.12	0.651	0.636	0.634	0.615	0.616	0.600	0.592	0.577	0.592	0.577	0.578	0.559	0.578	0.559	0.578
1.14	0.685	0.667	0.670	0.649	0.655	0.632	0.633	0.615	0.633	0.615	0.621	0.600	0.621	0.600	0.621
1.16	0.715	0.694	0.702	0.678	0.689	0.663	0.669	0.647	0.669	0.647	0.659	0.632	0.659	0.632	0.659
1.18	0.738	0.718	0.728	0.706	0.715	0.692	0.697	0.677	0.697	0.677	0.690	0.667	0.690	0.667	0.690
1.20	0.758	0.741	0.749	0.728	0.738	0.719	0.721	0.703	0.721	0.703	0.715	0.694	0.715	0.694	0.715
1.30	0.833	0.819	0.827	0.811	0.821	0.803	0.808	0.795	0.808	0.795	0.806	0.790	0.806	0.790	0.806
1.40	0.878	0.872	0.874	0.865	0.869	0.860	0.859	0.855	0.859	0.855	0.859	0.852	0.859	0.852	0.859
1.50	0.909	0.907	0.907	0.902	0.903	0.899	0.894	0.894	0.894	0.894	0.895	0.892	0.895	0.892	0.895
1.60	0.934	0.932	0.933	0.928	0.931	0.926	0.922	0.923	0.922	0.923	0.924	0.926	0.924	0.926	0.924
1.70	0.950	0.949	0.949	0.947	0.950	0.949	0.941	0.945	0.941	0.945	0.943	0.949	0.943	0.949	0.943
1.80	0.962	0.962	0.962	0.962	0.962	0.962	0.962
1.90	0.973	0.973	0.972	0.972	0.972	0.972	0.972
2.00	0.981	0.981	0.980	0.980	0.980	0.978	0.978
3.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000
6.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000
8.00	1.004	1.004	1.004	1.004	1.004	1.004	1.004
10.00	1.007	1.007	1.007	1.007	1.007	1.010	1.010
15.00	1.010	1.010	1.010	1.010	1.010	1.020	1.020

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

p_r	1.50		1.60		1.70		1.8		1.9		2.0		2.2	
	W		W		W		W		W		W		W	
	II	I	II	I	II	I	II	I	II	I	II	I	II	I
z	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27	0.23	0.27
T_r														
0.50	0.221	0.274	0.236	0.293	0.251	0.311	0.329	0.347	0.365	0.383	0.402	0.426	0.454	0.488
0.60	0.192	0.243	0.205	0.259	0.217	0.275	0.291	0.307	0.323	0.341	0.358	0.376	0.394	0.412
0.70	0.175	0.224	0.186	0.239	0.196	0.254	0.268	0.282	0.297	0.311	0.326	0.341	0.356	0.371
0.80	0.166	0.215	0.177	0.229	0.187	0.243	0.257	0.270	0.284	0.298	0.312	0.326	0.341	0.355
0.90	0.167	0.217	0.179	0.230	0.189	0.244	0.257	0.270	0.283	0.297	0.311	0.325	0.339	0.353
0.92	0.169	0.219	0.182	0.233	0.192	0.246	0.259	0.272	0.285	0.299	0.312	0.326	0.340	0.354
0.94	0.171	0.223	0.184	0.237	0.194	0.249	0.262	0.275	0.288	0.301	0.314	0.327	0.341	0.354
0.96	0.177	0.230	0.191	0.242	0.197	0.255	0.267	0.279	0.291	0.303	0.315	0.327	0.340	0.353
0.98	0.184	0.241	0.199	0.253	0.203	0.265	0.276	0.287	0.298	0.309	0.320	0.331	0.342	0.353
1.00	0.191	0.247	0.200	0.254	0.209	0.268	0.279	0.293	0.306	0.319	0.332	0.345	0.358	0.371
1.01	0.198	0.258	0.206	0.262	0.215	0.277	0.287	0.300	0.312	0.324	0.336	0.348	0.360	0.372
1.02	0.208	0.273	0.214	0.276	0.222	0.288	0.296	0.308	0.319	0.330	0.341	0.352	0.363	0.374
1.03	0.222	0.288	0.224	0.289	0.229	0.300	0.307	0.319	0.329	0.340	0.351	0.361	0.372	0.383
1.04	0.246	0.308	0.239	0.305	0.241	0.312	0.317	0.326	0.335	0.344	0.353	0.362	0.371	0.380
1.05	0.286	0.332	0.262	0.323	0.258	0.328	0.332	0.338	0.341	0.344	0.347	0.350	0.353	0.356
1.06	0.333	0.368	0.293	0.347	0.278	0.346	0.347	0.349	0.351	0.353	0.355	0.357	0.359	0.361
1.07	0.387	0.398	0.334	0.370	0.307	0.365	0.365	0.364	0.361	0.358	0.355	0.352	0.349	0.346
1.08	0.429	0.431	0.378	0.396	0.342	0.387	0.380	0.375	0.372	0.368	0.364	0.360	0.356	0.352
1.09	0.466	0.464	0.418	0.424	0.380	0.409	0.398	0.390	0.386	0.382	0.378	0.374	0.370	0.366
1.10	0.504	0.496	0.460	0.455	0.419	0.432	0.416	0.408	0.400	0.394	0.388	0.382	0.376	0.370
1.12	0.563	0.542	0.526	0.505	0.486	0.480	0.454	0.439	0.432	0.426	0.420	0.414	0.408	0.402
1.14	0.609	0.580	0.577	0.549	0.541	0.521	0.494	0.479	0.466	0.454	0.442	0.430	0.418	0.406
1.16	0.649	0.619	0.621	0.588	0.588	0.565	0.540	0.521	0.503	0.488	0.474	0.460	0.446	0.432
1.18	0.680	0.653	0.651	0.622	0.626	0.606	0.583	0.561	0.542	0.525	0.508	0.492	0.476	0.460
1.20	0.707	0.682	0.685	0.653	0.652	0.638	0.620	0.600	0.573	0.556	0.539	0.522	0.505	0.488
1.30	0.801	0.783	0.784	0.768	0.770	0.755	0.742	0.731	0.716	0.697	0.678	0.659	0.640	0.621
1.40	0.856	0.846	0.843	0.837	0.832	0.829	0.819	0.812	0.801	0.786	0.770	0.754	0.738	0.722
1.50	0.895	0.888	0.883	0.872	0.874	0.877	0.869	0.861	0.852	0.842	0.832	0.822	0.812	0.802
1.60	0.926	0.919	0.914	0.894	0.909	0.909	0.904	0.896	0.888	0.880	0.870	0.860	0.850	0.840
1.70	0.952	0.940	0.935	0.916	0.931	0.932	0.929	0.922	0.915	0.908	0.900	0.892	0.884	0.876
1.80	0.956	0.932	0.949	0.946	0.940	0.935	0.930	0.924	0.918	0.912	0.906
1.90	0.953	0.962	0.960	0.956	0.952	0.947	0.942	0.937	0.932	0.927
2.00	0.976	0.974	0.972	0.971	0.969	0.966	0.963	0.960	0.957	0.954	0.951
3.00	0.999	0.997	0.997	0.995	0.991	0.986	0.984	0.981	0.978	0.975	0.972
4.00	1.000	1.000	1.000	0.997	0.993	0.990	0.988	0.986	0.984	0.982	0.980
6.00	1.004	1.003	1.005	1.000	0.994	0.995	0.993	0.991	0.989	0.987	0.985
8.00	1.008	1.008	1.008	1.005	0.998	0.998	0.996	0.994	0.992	0.990	0.988
10.00	1.010	1.010	1.012	1.008	1.000	0.998	0.996	0.994	0.992	0.990	0.988
15.00	1.020	1.020	1.020	1.020	1.020	1.020	1.020	1.020	1.020	1.020	1.020

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

TABLE D-12. COMPRESSIBILITY FACTORS z OF PURE GASES AND LIQUIDS (Continued)

pr	8.0		9.0		10		15		20		25		30
	II		II		II		II		II		II		II
	0.27		0.27		0.27		0.27		0.27		0.27		0.27
z_c													
T_R													
0.50	1.439	1.616	1.791	2.673	3.551	4.41	5.82						
0.60	1.262	1.415	1.568	2.337	3.098	3.85	4.59						
0.70	1.139	1.277	1.413	2.096	2.769	3.43	4.08						
0.80	1.056	1.180	1.305	1.922	2.525	3.12	3.70						
0.90	1.005	1.119	1.233	1.796	2.341	2.88	3.40						
0.92	0.997	1.110	1.222	1.774	2.310	2.83	3.35						
0.94	0.991	1.100	1.201	1.753	2.278	2.79	3.30						
0.96	0.985	1.090	1.202	1.734	2.250	2.76	3.25						
0.98	0.980	1.080	1.195	1.715	2.224	2.72	3.20						
1.00	0.976	1.074	1.193	1.704	2.200	2.69	3.15						
1.01	0.974	1.072	1.188	1.697	2.188	2.67	3.14						
1.02	0.973	1.069	1.184	1.688	2.175	2.66	3.11						
1.03	0.972	1.068	1.181	1.681	2.164	2.63	3.08						
1.04	0.972	1.066	1.177	1.672	2.153	2.61	3.06						
1.05	0.972	1.065	1.174	1.666	2.142	2.60	3.04						
1.06	0.971	1.064	1.171	1.658	2.130	2.58	3.02						
1.07	0.970	1.062	1.168	1.652	2.119	2.57	3.00						
1.08	0.970	1.061	1.165	1.646	2.109	2.55	2.96						
1.09	0.970	1.060	1.162	1.638	2.098	2.53	2.95						
1.10	0.970	1.060	1.160	1.631	2.088	2.51	2.93						
1.12	0.970	1.058	1.156	1.618	2.068	2.50	2.89						
1.14	0.970	1.058	1.153	1.606	2.049	2.46	2.85						
1.16	0.972	1.057	1.151	1.594	2.030	2.44	2.81						
1.18	0.973	1.056	1.150	1.584	2.013	2.41	2.78						
1.20	0.975	1.057	1.148	1.573	1.995	2.39	2.74						
1.30	0.984	1.063	1.144	1.528	1.921	2.27	2.63						
1.40	0.996	1.071	1.144	1.496	1.862	2.19	2.56						
1.50	1.012	1.081	1.146	1.476	1.818	2.15	2.56						
1.60	1.028	1.092	1.150	1.461	1.790	2.12	2.49						
1.70	1.041	1.100	1.154	1.448	1.767	2.09	2.44						
1.80	1.052	1.108	1.156	1.435	1.744	2.05	2.39						
1.90	1.061	1.115	1.158	1.420	1.714	2.02	2.33						
2.00	1.070	1.120	1.159	1.400	1.691	1.99	2.29						
3.00	1.068	1.107	1.130	1.310	1.500	1.67	2.24						
4.00	1.065	1.099	1.120	1.255	1.400	1.53	2.16						
6.00	1.064	1.089	1.100	1.200	1.300	1.42	1.66						
8.00	1.063	1.082	1.085	1.170	1.250	1.32	1.50						
10.00	1.062	1.077	1.080	1.130	1.185	1.24	1.40						
15.00	1.061	1.070	1.070	1.100	1.140	1.17	1.30						

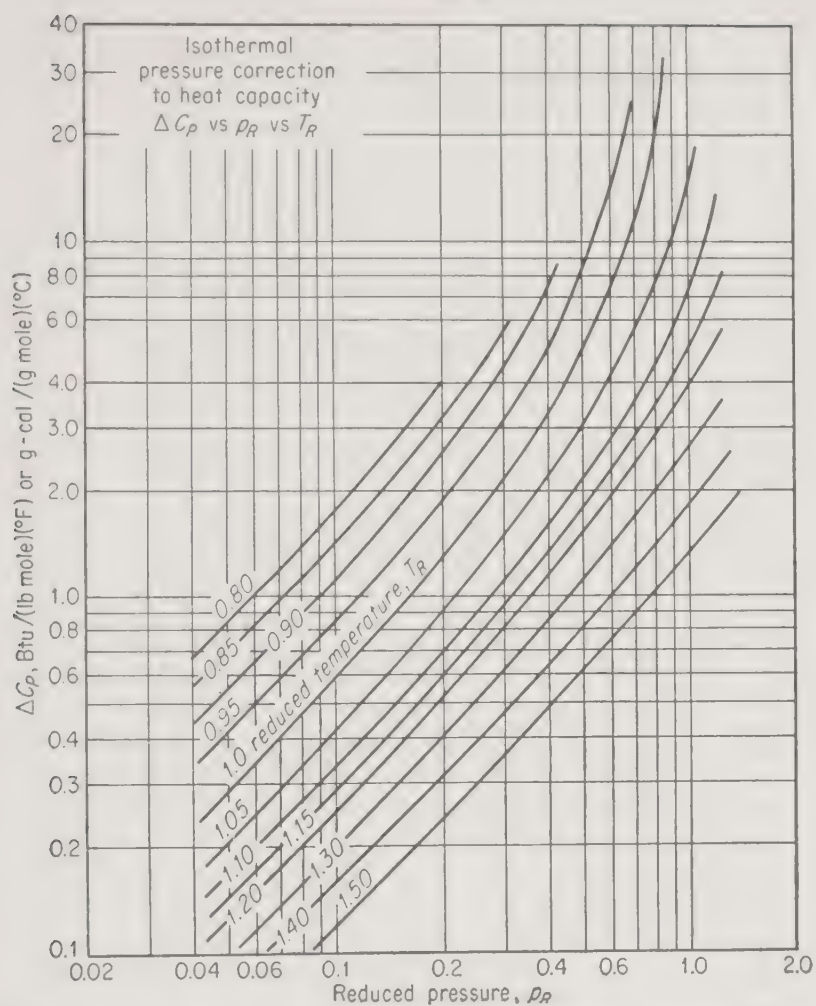


FIG. D-1. Generalized ΔC_p for isentropic temperature change. [From W. C. Edminster, *Ind. Eng. Chem.*, **30**:352 (1938).]

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NOTE: The properties of gases and liquids are recorded in numerous articles. These frequently include tables and charts of pVT data, thermodynamic properties, and phase-equilibrium information. The references given below cover reviews, bibliographies, or limited compilations of such data.

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APPENDIX E

EQUIPMENT SIZES

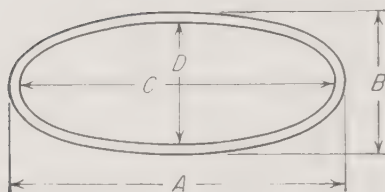


TABLE E-1. DIMENSIONS OF BOURDON TUBES†

Gauge dial, in.	Pressure, psi	A, mm	B, mm	C, mm	D, mm	Over-all length of tube, mm
4	1,000	13.9	6.5	11.8	5.0	120
	2,000	12.7	5.6	11.1	4.9	120
	3,000	12.4	6.5	10.5	4.6	120
	5,000	13.8	6.7	11.5	4.4	120
	4 tons	13.4	7.0	10.1	3.7	120
5	800	13.0	5.9	11.4	4.3	150
	2,000	13.3	6.5	12.3	4.5	150
	3,000	12.4	7.4	10.0	5.0	150
	4 tons	11.7	7.3	9.0	4.6	150
6	1,000	16.2	8.7	14.2	6.7	180
	2,000	17.2	8.9	14.0	6.6	180
	3,000	16.3	8.0	13.7	5.4	180
	8 tons	10.8	7.3	6.5	3.0	180

† From D. M. Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressure," Oxford University Press, New York, 1940.

Information on pipe and fittings may be found in J. H. Perry, editor, "Chemical Engineers' Handbook," third edition, pages 413 to 454, McGraw-Hill Book Company, Inc., New York, 1950. Reference can be made to the "Code for Pressure Piping," ASA B 31.1-1942 with supplements B 31.1a-1944 and B 31.1b-1947 (American Standards Association, New York) and also to Crocker, "Piping Handbook," fourth edition, McGraw-Hill Book Company, Inc., New York, 1945

TABLE E-2. HIGH-PRESSURE TUBING SIZES

Tubing is available in a number of sizes. Some have solid walls; others have composite walls with liners or thin cores of metals such as copper, silver, platinum, stainless steel, and others, with the outer layer of less expensive common metals. The sizes considered somewhat standard are:

<i>in. O.D.</i>	<i>in. I.D.</i>
$\frac{1}{8}$	0.024
$\frac{1}{4}$	$\frac{1}{16}$
$\frac{1}{4}$	$\frac{3}{32}$
$\frac{5}{16}$	0.050
$\frac{5}{16}$	$\frac{1}{16}$
$\frac{3}{8}$	$\frac{1}{8}$
$\frac{1}{2}$	$\frac{1}{8}$
$\frac{9}{16}$	$\frac{3}{16}$
$\frac{3}{4}$	$\frac{1}{16}$
$\frac{3}{4}$	$\frac{1}{4}$
$1\frac{5}{16}$	$\frac{5}{16}$
$1\frac{1}{4}$	$\frac{3}{8}$
$1\frac{1}{2}$	$\frac{1}{2}$

Typical Commercial Sources: Harwood Engineering Company, Inc.; American Instrument Company, Inc.; Autoclave Engineers Inc.

APPENDIX F

LIMITS OF FLAMMABILITY OF GASES AND VAPORS

A flammable mixture of gases, such as methane and air, may be diluted with one of its constituents or with other gases until it is no longer flammable. The dilution limit of flammability, or simply the limit of flammability, is the borderline composition; a slight change in one direction produces a flammable mixture, in the other direction a nonflammable mixture.

There are clearly two limits of flammability, a lower and a higher, for each pair of so-called combustible gases and supporters of combustion. The lower limit corresponds to the minimum amount of combustible gas, and the higher or upper limit to the maximum amount of combustible gas capable of conferring flammability on the mixture. For example, for methane-air mixtures these limits under normal conditions are approximately 5 and 14 per cent methane, respectively. Mixtures within these limits liberate enough energy on combustion of any one layer to ignite the neighboring layer of unburned gas and are therefore capable of self-propagation of flame; others are not. Mixtures richer than 14 per cent methane, however, may burn on contact with external air, for mixtures that contain less than 14 per cent methane are formed in the zone where the gases mingle.¹

The limits of flammability are affected by the source of ignition, the direction of flame propagation (upward, downward, horizontally, or radially in a sphere), the size and shape of the vessel, the initial pressure, the initial temperature, the extent of turbulence of the mixture, and the presence of inert gases. The effects of these conditions are discussed by Coward and Jones. Some mixtures near the limits of flammability will transmit flame upward but not downward, and for safety considerations measurements made in the upward direction are best considered as establishing the danger line.

Increase of pressure above that of the atmosphere does not always widen the limits.² On the contrary, the range of flammability of some mixtures is narrowed by increase of pressure, so that a mixture that can propagate flame at atmospheric pressure may not be able to do so at higher pressures. For such mixtures the lower limit may pass through a minimum and the higher limit through a maximum at pressures (not necessarily the same) equal to or greater than that of the atmosphere.

Attention may be called to the observations that the range of flammability of hydrogen-air and carbon monoxide-air mixtures (downward propagation of flame) is narrowed at both limits by moderate increases of pressure above atmospheric and that under the same conditions the range of each of the gases of the paraffin series, with air, is narrowed at the lower-limit side (by moderate increase of pressure beyond a certain critical value) but widened at the higher-limit side.³

¹ The discussion in Appendix F is based on H. F. Coward and G. W. Jones, Limits of Flammability of Gases and Vapors, *U.S. Bur. Mines Bull.* 503 (1952).

² E. Berl and G. Werner, *Z. angew. Chem.*, **40**:245 (1927).

³ H. F. Coward and G. W. Jones, *loc. cit.*

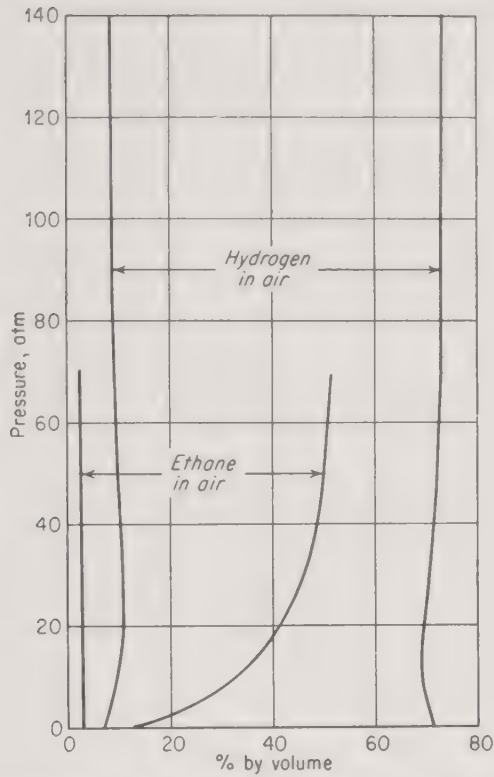


FIG. F-1. Effects of pressure on the upper and lower limits of flammability for mixtures of hydrogen and air and for mixtures of ethane and air. [From H. F. Coward and G. W. Jones, *U.S. Bur. Mines Bull.* 503 (1952).]

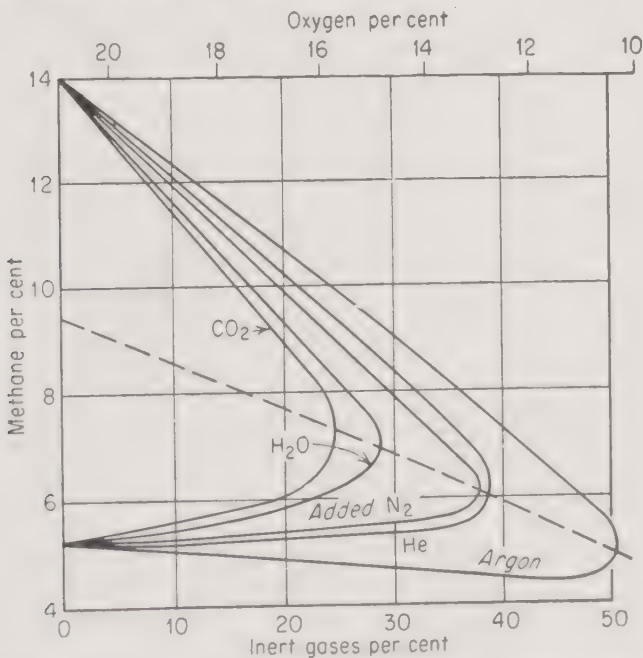


FIG. F-2. Limits of flammability of methane in air with added carbon dioxide, water vapor, nitrogen, helium, and argon. [From H. F. Coward and G. W. Jones, *U.S. Bur. Mines Bull.* 503 (1952).]

TABLE F-1. LIMITS OF FLAMMABILITY IN AIR AND OXYGEN†

Gas or vapor	Limits in air, %		Limits in oxygen, %	
	Lower	Higher	Lower	Higher
Hydrogen.....	4.0	75	4.0	94
Ammonia.....	15	28	15	79
Hydrazine.....	4.7	100		
Hydrogen cyanide.....	6	41		
Cyanogen.....	6	32		
Carbon disulfide.....	1.25	44		
Carbon monoxide.....	12.5	74	15.5	94
Methane.....	5.3	14	5.1	61
Ethane.....	3.0	12.5	3.0	66
Propane.....	2.2	9.5	2.3	55
Butane.....	1.9	8.5	1.8	49
Isobutane.....	1.8	8.4	1.8	48
Pentane.....	1.5	7.8		
Hexane.....	1.2	7.5		
Dimethyl butane.....	1.2	7.0		
Octane.....	1.0			
Ethylene.....	3.1	32	3.0	80
Propylene.....	2.4	10.3	2.1	53
Butylene.....	2.0	9.6		
Butene-1.....	1.6	9.3	1.8	58
Butadiene.....	2.0	11.5		
Acetylene.....	2.5	81		
Benzene.....	1.4	7.1		
Toluene.....	1.4	6.7		
Styrene.....	1.1	6.1		
Cyclopropane.....	2.4	10.4	2.5	60
Methyl alcohol.....	7.3	36		
Ethyl alcohol.....	4.3	19		
Methyl ether.....	3.4	18	3.9	61
Ethyl ether.....	1.9	48	2.0	82
Ethyl <i>n</i> -propyl ether.....	1.9	24	2.0	78
Isopropyl ether.....	1.4	21		69
Ethylene oxide.....	3.0	80		
Propylene oxide.....	2.1	21.5		
Acetaldehyde.....	4.1	55	4	93
Acrolein.....	2.8	31		
Furfural.....	2.1			

TABLE F-1. LIMITS OF FLAMMABILITY IN AIR AND OXYGEN† (Continued)

Gas or vapor	Limits in air, %		Limits in oxygen, %	
	Lower	Higher	Lower	Higher
Acetone	3.0	11		
Methyl formate.....	5.9	20		
Ethyl formate.....	2.7	13.5		
Ethyl acetate.....	2.5	9		
Vinyl acetate.....	2.6	13.4		
Methylamine.....	4.9	20.7		
Dimethylamine.....	2.8	14.4		
Trimethylamine.....	2.0	11.6		
Ethylenimine.....	3.6	46		
Methyl chloride.....	10.7	17.4	8	<u>66</u>
Ethyl chloride.....	3.8	15.4	4.0	67
Vinyl chloride.....	4.0	22	4.0	70
Dichloroethylene.....	9.7	12.8	10	26
Dimethyl sulfide.....	2.2	19.7		
Pittsburgh natural gas.....	<u>4.8</u>	<u>13.5</u>		
Gasoline.....	1.4	<u>7.6</u>		
Coal gas.....	<u>5.3</u>	<u>32</u>	7	70
Producer gas.....	20-35	70-80		

† From H. F. Coward and G. W. Jones, Limits of Flammability of Gases and Vapors, *U.S. Bur. Mines Bull.* 503 (1952).

The effects of pressure on the upper and lower limits for mixtures of hydrogen and air and for mixtures of ethane and air⁴ are shown in Fig. F-1.

The range of flammability is widened by an increase in the initial temperature. The lower limit should be decreased by a rise in temperature, and the higher limit should be increased. The addition of increasing amounts of chemically inert gases to mixtures with air causes the limits to approach and ultimately to meet. This behavior is shown in Fig. F-2, where the percentages of several inert gases in the preignition mixture are shown on the abscissa and the limits of flammability are shown on the ordinate. The dotted line represents the stoichiometrical mixture for complete combustion.

Table F-1 includes the upper and lower limits in air and oxygen for a list of gases, vapors, and mixtures selected from the more extensive table prepared by Coward and Jones. The numbers underlined are less reliable because they were not measured with upward flame travel or for some other reason. Additional information may be found in the literature.^{1,2,4}

⁴ R. E. Kennedy, I. Spolan, W. K. Mock, and G. S. Scott, *U.S. Bur. Mines Rept. Invest.* 4751 (1950).

APPENDIX G

MERCURY-CLEANING TECHNIQUES

Mercury is indispensable for precise scientific measurements. Its high density, negligible vapor pressure, and the insolubility of gases in it are some of its desirable properties. Mercury is not readily oxidized under ordinary conditions when it is pure. This must be due to a very slow rate of oxidation since mercury oxide is also stable. However, the merest traces of metals dissolved in mercury change its surface properties markedly. It is then easily tarnished, forms small globules which do not coalesce, wets glass and other substances, and takes on a dirty appearance. This effect is produced by both base metals and by silver, gold, or platinum. It is possible that the foreign metal catalyzes the oxidation of the mercury. Mere traces of foreign metals have a remarkable effect and seriously interfere with the use of mercury in instruments and measurements. With the exception of recent uses for other metals, a higher degree of purity has been required for mercury than for any other substance.

The usual contamination of mercury is due to its property of dissolving or amalgamating with other metals. Some metals are readily oxidized, such as zinc, cadmium, bismuth, tin, copper, lead, etc., while others like silver, gold, and platinum are not. The latter have much lower vapor pressures than mercury and may be readily separated from it by distillation. The baser metals in general have higher vapor pressures and distill over with the mercury. The baser metals may be changed to oxides, which have negligible vapor pressures, or may be removed by acid containing dissolved mercury salts. The electropositive metals such as zinc and cadmium will displace the mercury from solution. However, this is a reversible electrochemical reaction and cannot be complete for all metals. Experiments have shown that the vapors of the base metals are readily oxidized but that excessively long periods are required when oxidation of the metals in the liquid is carried out by bubbling air through the amalgam. The situation encountered in purifying mercury is represented by the following:

1. The base metals are not readily separated by distillation because of their high vapor pressures.
2. The base metals may be removed by contact with an acid-mercury solution, but there is no assurance that the removal will be complete.
3. Complete oxidation of the base-metal vapors has been shown to take place at 200°C with 25 mm of air partial pressure or 5 mm of oxygen. The vapors of silver, gold, and platinum are not affected.
4. Mercury vapor does not oxidize readily at 200°C with a partial pressure of oxygen less than 5 mm. Mercury oxide appears when the partial pressure of oxygen is higher than this.

5. The vapor pressures of silver, gold, and platinum are very low, but traces of these metals are found in the distillate and complete removal requires three successive distillations.

6. Oxygen and air are completely insoluble in mercury for all practical purposes.

7. The merest trace of foreign metals in mercury causes it to oxidize or tarnish, but with really pure mercury absorption of oxygen or oxidation does not occur.

A distillation technique is described by G. A. Hulett¹ in which separation of both the base and noble metals from mercury is effectively carried out. A small stream of air is allowed to bubble up through the mercury in the still and passes over with the vapors. This arrangement also avoids the troublesome bumping and spurting of the mercury which takes place when a little air is present. The pressure in the still is maintained at 20 to 30 mm and the temperature at about 200°C. The vapors of the base metals are completely oxidized under these conditions, and the oxides collect on the distillate when they are present in considerable quantity. The distillate then has a dirty appearance, but when it is filtered through a pinhole in a filter paper it is then free from other metals provided sufficient air has passed over with the vapors. If silver, gold, or platinum is present, the distillation should be repeated.

A still arranged for continuous operation is shown in Fig. G-1. The still consists of a flask *a* about 15 cm in diameter with the glass tube *e* sealed in the bottom. This tube connects to the reservoir *h*. The cock *g* is ordinarily open but is necessary. Air is admitted from below the still through the side tube *s* which is attached by the ground-glass joint *f*. The side tube ends in a capillary which delivers the air well into the tube *e* where it bubbles up through the mercury and into the still. The oxygen rate may be observed and controlled by the stopcock *i*. Mercury is added to the reservoir *h* at the rate it is to enter the flask *a*. The large U tube *c* is made from 25-mm thin-walled glass tubing and is 50 cm long, thus giving a condenser for the mercury vapor 1 m long. The tube *o* is connected to a vacuum source. Mercury condenses in the tube *c*, collects in the tube *d*, and flows out at the bent-up end. Tube *d* is about a meter long and is 4 mm in diameter. The electric heating mantel for the still is shown at *b*.¹

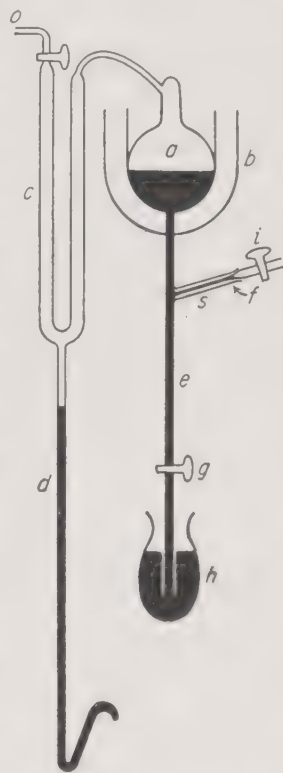


FIG. G-1. Mercury still. [From G. A. Hulett, *Phys. Rev.*, **33**:312 (1911).]

¹ This discussion is based on G. A. Hulett, *Phys. Rev.*, **33**:312 (1911).

APPENDIX H

STEELS AND ALLOYS FOR HIGH PRESSURES

A partial list of steels and alloys which have been used in high-pressure service is given in Table H-1. For information on other alloys and for more details as to the properties and uses of those listed, consult other sources.¹⁻⁴

A brief classification of a limited list of steels and alloys is helpful in giving the uninitiated a preliminary orientation in a complex field. The selection of an alloy for a given application requires that numerous factors present in each case be considered. Since only a few of these factors are listed here, this section avoids making specific recommendations.

Steels

1. Carbon steels.

A. Carburizing grades such as AISI (or SAE) C1015, C1022, and C1118.

These are used primarily when an external case of considerably greater hardness than the interior is required and are not suitable for pressure-vessel walls.

B. Water- and oil-hardening grades. These are the more commonly used carbon steels where strength as influenced by the carbon content is the main factor. Hardenability is low, and after heat treating, the strength at the center is considerably less than at the surface. Use for thick cross sections as in pressure vessels is thus to be avoided. Examples are AISI C1030, C1040, C1050, C1060, C1080, C1095.

2. Low-alloy steels. These steels contain a few per cent of alloying elements primarily to increase hardenability and permit the use of thicker cross sections. Very high tensile strengths are possible after proper heat treatment. The principal elements used to increase hardenability are nickel and chromium which promote stability of the martensitic structure. Corrosion resistance is superior to that of the carbon steels, but, if corrosion is the controlling feature, the higher-alloy steels should be used.

A. Carburizing grades. These are primarily used when a hardened case of increased carbon content is desired. The distinguishing feature is the

¹ N. E. Woldman, "Engineering Alloys Names Properties Uses," American Society for Metals, 1954.

² Carl A. Zapffe, "Stainless Steels," The American Society for Metals, 1949.

³ See references in Chap. 3.

⁴ "Modern Steels and Their Properties," Handbook 268-B, Bethlehem Steel Company, 3d ed., 1955.

carbon, nickel, and chromium content. Examples are AISI E3310, 4820, and 8620.

- B. Water-hardening grades. These low-alloy steels are of medium hardenability and require the more extreme water quench to produce the desired hardness. Examples: AISI 2330 and 8630.
- C. Oil-hardening grades. These low-alloy steels possess such a high hardenability that an oil quench is sufficient to induce the desired hardness. A remarkable range of physical properties is exhibited with tensile strengths of better than 300,000 psi. Examples of this grade listed in decreasing order of hardenability are AISI 4340, 9255, 1340, 6152, 3140, 4150, 5150, 4063, 9261. The list arranged in decreasing order of maximum tensile strength ($\frac{1}{2}$ -in. rod, 1000°F draw) is AISI 9261, 6152, 4063, 9255, 4150, 4340, 5150, 3140, 1340. The steel AISI 4340 ranks relatively high in tensile strength for a 1000°F draw. The 1000°F draw produces greater ductility than do lower temperatures and is thus a better draw temperature. The high strength of the 4340 at a 1000°F draw and its great hardenability lead to its selection for high-pressure-vessel walls.
3. Stainless steels. These steels may be placed in three classes on the basis of their chromium and nickel contents.

Class I. Chromium is present in amounts from 11.5 to 18 per cent and is the only major alloying element, with carbon as the next. These are martensitic steels after heat treatment and exhibit considerable hardening upon heat treatment. Examples: AISI 403 and 410 are used extensively for steam-turbine blades. AISI 416 is similar to 410 with an increase in sulfur and selenium to increase machinability. AISI 431 is the most corrosion-resistant of Class I.

Class II. Chromium is present in amounts from 11.5 to 27 per cent and is the only major alloying element. These are ferrite steels and exhibit little or no hardening upon heat treatment. Due to this lack of hardenability either by heat treatment or by work hardening this class is not used in high-pressure structural applications. Class I and II belong to the AISI 400 series. Examples: AISI 405 is especially adaptable for welding and may be used as a liner for high-pressure vessels. AISI 406 is used for oxidation resistance at high temperatures (contains 4 per cent Al). AISI 430 is particularly resistant to nitric acid. AISI 430F is a modification of 430 with much better machinability. Over certain ranges of their compositions 430 and 430F may be hardened by heat treatment and increased strength is obtained.

Class III. Chromium is present in amounts from 16 to 26 per cent and nickel from 6 to 22 per cent with the carbon content held low. These steels are austenitic. Great increases in strength may be obtained by work hardening which transforms the austenite to martensite at ordinary temperatures by plastic deformation (cold working). Class III belongs to the AISI 300 series. Examples: AISI 301 has the lowest alloy content in class III and work hardens to the maximum extent. AISI 302 is the common 18-8 stainless steel

(Continued on page 526)

TABLE H-1. A PARTIAL LIST OF STEELS AND ALLOYS USED
IN HIGH-PRESSURE SERVICE
(See also Table 6-3)

Designation	Composition, %	Approximate maximum strength after hardening†		Remarks
		Tensile strength, psi	Yield point, psi	
C1015.....	0.13–0.18 C, 0.30–0.60 Mn, 0.04 max. P, 0.05 max. S, 0.17 Si, bal. Fe	75,000	44,000	Not used for pressure vessels
C1050.....	0.48–0.55 C, 0.60–0.90 Mn, 0.04 max. P, 0.05 max. S, 0.19 Si	160,000	115,000	Not used for pressure vessels
A4340.....	0.38–0.43 C, 0.60–0.80 Mn, 0.04 max. P, 0.04 max S, 0.20–0.35 Si, 1.65–2.00 Ni, 0.70–0.90 Cr, 0.20–0.30 Mo, bal Fe	1½-in. rod, 400°F draw 280,000	225,000	
		1-in. rod, 1000°F draw 175,000	165,000	
A6150.....	0.48–0.53 C, 0.65–0.90 Mn, 0.04 max. P, 0.04 max. S, 0.20–0.35 Si, 0.80–1.10 Cr	1-in. rod, 1000°F draw 173,500	167,750	
E52100.....	0.95–1.10 C, 0.25–0.45 Mn, 0.025 max. P, 0.025 max. S, 0.20–0.35 Si, 1.30–1.60 Cr			
✓ Stainless steel 410	0.15 max. C, 11.5–13.5 Cr,	200,000	150,000	
Stainless steel 416	0.15 max. C, 12–14 Cr, bal. Fe	200,000	150,000	
Stainless steel 431	0.20 max. C, 15–17 Cr, 1.25–2.50 Ni, bal. Fe	220,000	185,000	
Stainless steel 405	0.08 max. C, 11.5–13.5 Cr, 0.10–0.30 Al, bal. Fe	60,000	35,000	
Stainless steel 406	0.15 max. C, 12–14 Cr, 3.5–4.5 Al, bal. Fe	85,000		
Stainless steel 430	0.12 max. C, 14–18 Cr, bal. Fe	65,000	35,000	
Stainless steel 431	0.20 max. C, 15–17 Cr, 1.25–2.50 Ni	195,000	165,000	
Stainless steel 301	0.08–0.20 C, 16–18 Cr, 6–8 Ni, bal. Fe	100,000	40,000	
Stainless steel 302	0.08–0.20 C, 17–19 Cr, 8–10 Ni, bal. Fe	85,000	35,000	

† It is usually hazardous to heat-treat steel used for pressure vessels to its maximum strength if this results in extreme hardness (above about 35 to 40 Rockwell C) because the steel is then brittle.

TABLE H-1. A PARTIAL LIST OF STEELS AND ALLOYS USED IN HIGH-PRESSURE SERVICE (Continued)

Designation	Composition, %	Approximate maximum strength after hardening		Remarks
		Tensile strength, psi	Yield point, psi	
Stainless steel 302B.....	0.08-0.20 C, 17-19 Cr, 8-10 Ni, 2-3 Si, bal. Fe	95,000	40,000	
Stainless steel 303	0.15 max. C, 17-19 Cr, 8-10 Ni, >0.07 P, S, or Se, <0.60 Mo or Zr, bal. Fe	85,000	35,000	
Stainless steel 310	0.25 max. C, 24-26 Cr, 19-22 Ni, 1.50 max. Si, bal. Fe	90,000	40,000	
Stainless steel 316	0.10 max. C, 16-18 Cr, 10-14 Ni, 2-3 Mo, bal. Fe	80,000	35,000	
Stainless steel 347	0.08 max. C, 17-19 Cr, 9-12 Ni, 10 × C (min.) Cb, bal. Fe	85,000	35,000	
Hastelloy A (Haynes-Stellite Div. Union Carbide Carbon Co.)...	23 max. Mo, 23 max. Fe, bal. Ni	110,000-120,000	47,000-52,000	Resists HCl and H ₂ SO ₄
Hastelloy B (Haynes-Stellite Div. Union Carbide and Carbon Co.).....	26-30 Mo, 4-6 Fe, 0.12 max. C, 62 Ni	Rolled 140,000 65,000		Resists HCl and hot H ₃ PO ₄
Inconel ✓ (International Nickel Co.)....	11-15 Cr, 70 min. Ni, 1.0 max. Mn, 10 max. Fe, 0.5 max. Si, 0.15 max. C	Annealed 80,000-95,000 30,000-40,000		Corrosion-resistant, heat- and oxidation-resistant
		Cold drawn 110,000-115,000 80,000-95,000		
		Cast 65,000 30,000		
Monel ✓ (International Nickel Co.)....	23 min. Cu, 60 min. Ni, 3.5 max. Fe, 3.5 max. Mn, 0.30 max. C, 0.5 max. Al, 0.5 max. Si	Hot rolled 95,000 65,000		Corrosion-resistant, high-impact-resistant
		Cold drawn 125,000 95,000		

TABLE II-1. A PARTIAL LIST OF STEELS AND ALLOYS USED IN HIGH-PRESSURE SERVICE (Continued)

Designation	Composition, %	Approximate maximum strength after hardening		Remarks
		Tensile strength, psi	Yield point, psi	
TAM Metallic titanium (Titanium Alloy Mfg. Div. National Lead Co.).....	>98 Ti, <0.2 Fe, <0.2 Si, <0.2 C, <0.2 Al			Corrosion-resistant
Ampeco 18-22 (Ampeco Metal Inc.).....	10.6-11.2 Al, 3.4-4.0 Fe, bal. Cu	90,000-100,000	45,000-55,000	For bearing, wear-resistant, heat-treatable
Uniloy 19-9WMo (Universal Cyclops Steel Co.)	0.08-0.12 C, 0.4-1.0 Mn, 18-20 Cr, 1-1.75 W, 0.8-10 Ni, 0.2-0.5 Mo, 0.3-0.6 Cb + Ta, 0.2-0.5 Ti, bal. Fe	85,000-150,000	50,000-120,000	For high-temperature use, corrosion- and heat-resistant, creep-resistant
N-155 (Universal Cyclops Steel Co.) (also Haynes-Stellite Div. Union Carbide and Carbon Co.).....	0.1-0.2 C, 1-2 Mn, 1 max. Si, 20-22 Cr, 1.75-2.75 W, 19-21 Ni, 2.5-3.5 Mo, 18.5-21 Co, 0.75-1.25 Cb, bal. Fe	80,000-150,000	40,000-110,000	Corrosion- and heat-resistant, creep-resistant
Carboloy (Carboloy Dept. of General Elec. Corp.).....	3-13 Co, bal. Tungsten Carbide	250,000-290,000	For cutting tools, very hard alloy, high strength

TABLE II-1. A PARTIAL LIST OF STEELS AND ALLOYS USED IN HIGH-PRESSURE SERVICE (*Continued*)

Designation	Composition, %	Approximate maximum strength after hardening		Remarks
		Tensile strength, psi	Yield point, psi	
Discaloy (Westinghouse Elec. Corp.) . . .	0.08 max. C, 12-15 Cr, 24-28 Ni, 2.5-3.5 Mo, 1.3-1.8 Ti, 0.6 Al, bal. Fe	130,000	85,000	High-temperature-resistant, high creep strength
Uniloy S-816 (Universal Cyclops Steel Co.)	0.32-0.42 C, 1-2 Mn, 1 max. Si, 19-21 Cr, 3.5-4.5 W, 19-21 Ni, 3.5-4.5 Mo, 40 min. Co, 3.5-4.5 Cb, bal. Fe	125,000-145,000	55,000-75,000	Corrosion- and heat-resistant
Nickel grade A (Internat. Nickel Co.)	99.4 Ni + Co, 0.10 Cu, 0.15 Fe, 0.15 Mn, 0.10 Si	65,000	25,000	Heat- and corrosion-resistant
Midvaloy BTG (Midvale Co.)	60 Ni, 12 Cr, 1.2 Mn, 0.3 C, 3.0 W, bal. Fe	Wrought 106,000 50,000		Austenitic, heat-resistant, for NH ₃ synthesis converters
Inconel X (International Nickel Co.)	0.08 max. C, 1.0 Mn, 9 Fe, 0.55 Si, 0.2 Cu, 14-16 Cr, 2.2-2.7 Ti, 0.4-1.0 Al, 0.7-1.2 Cb, bal. Ni	Annealed 115,000 55,000 Hardened 185,000 135,000		
Elastuf 44 (Horace T. Potts Co.)	0.5 C, Cr, Ni, Mo, bal. Fe	185,000-220,000	160,000-200,000	Nonmagnetic, high strength
Rezistal 416 (Crucible Steel Co. of America)	0.15 max. C, 12-14 Cr, 0.07 min. Se, 0.6 max. Mo, bal. Fe	Annealed 85,000 45,000 Hardened 185,000 155,000		

TABLE H-1. A PARTIAL LIST OF STEELS AND ALLOYS USED IN HIGH-PRESSURE SERVICE (Continued)

Designation	Composition, %	Approximate maximum strength after hardening		Remarks
		Tensile strength, psi	Yield point, psi	
✓ Ni-Span C.....	41-43 Ni, 2.4 Ti, 5.1-5.7 Cr, 0.06 max. C, 0.6 Al, 0.8 Si, bal. Fe	200,000	180,000	For instrument springs and diaphragms, constant modulus
✓ K-Monel.....	66 Ni, 30 Cu, 3.5 Al, 1.5 Fe, 0.20 max. C, 5 max. other metals	120,000-160,000	80,000-120,000	Nonmagnetic, for springs, check valves, etc.
Potomac.....	0.33C, 0.85 Si, 1.25 W, 5 Cr, 0.2 V, 1.5 Mo, bal. Fe	Ultimate strength: 750°F, 247,000 psi 1000°F, 215,000 psi
Kennametal	W, TiC, Co	Cutting tools, a cemented carbide
✓ Kentanium	TiC	135,000	Valve seats, resists heat, corrosion, wear, and thermal shock
Beryllium copper	1.5-2.25 Be, bal. Cu	180,000	Age-hardening, corrosion-resistant, nonmagnetic

and has very good corrosion resistance, is well fitted for most fabrication processes, and is the most widely used stainless steel. AISI 303 is a modification of 302 which has better machinability at the expense of corrosion resistance. In AISI 302-B the addition of silicon to 302 has given improved resistance to oxidation and carburization at high temperatures and particular resistance to sulfuric acid. AISI 310 has perhaps the greatest corrosion resistance of class III. AISI 347 is the best welding alloy of class III.

Special Alloys. These alloys are described briefly in Sec. 3-4, and a number of examples are included in Table H-1.

PROBLEMS AND QUESTIONS

Chapter 1

1-1. State briefly what you understand to be the chief reason for employing elevated pressure in the following cases. Explain your answers. (a) The synthesis of methanol. (b) The isomerization of hydrocarbons. (c) The storing of propane and butane. (d) The repressuring of oil wells with gas.

Chapter 2

2-1. Prepare a table listing the catalysts which are effective in three major classes of reactions such as alkylation, amination, and hydrogenation.

2-2. Select five reactions shown in this chapter which are employed on a large scale in industrial production.

2-3. Prepare lists of reactions selected from this chapter which have an important bearing on the industrial processing of raw materials derived from each of the following sources: (a) petroleum, (b) coal, (c) vegetable oils.

2-4. Select three reactions from those listed in this chapter, and describe in some detail the apparatus and method of operation to be employed in carrying out the reaction; one reaction should be carried out below 50 atm, one between 50 and 500 atm, and one somewhat above 500 atm.

Chapter 3

3-1. Select a steel or alloy for each of the applications below.

a. A pressure vessel for use in a commercial reactor. The metal wall will be exposed to hydrogen and nitrogen at 200°F and 300 atm.

b. A cylinder for a dead-weight gauge for use at pressures up to 50,000 psi.

c. A vessel to contain a mixture of hydrogen and helium at 200°F and 5,000 atm.

d. A vessel to store liquid methane at atmospheric pressure.

A list of steels is given in Table H-1. Indicate the chemical composition, yield strength, ultimate strength, and other special properties such as corrosion resistance, ductility, and the like, of the steels selected.

3-2. State briefly the meaning and significance of the terms hardenability, ferrite, cementite, austenitic, martensite, residual stresses, killed, rimmed, autofrettage, and precipitation hardening.

Chapter 4

4-1. Estimate the thickness of a reinforced-concrete barricade which will resist penetration by a slug of steel ejected from an exploding pressure vessel. For the purpose of this problem consider a cylindrical slug 1 in. in diameter and 3 in. long which is acted on by a steady pressure of 1,000 atm on one end as it starts from rest and is displaced a distance of 3 in. before attaining free flight.

4-2. Lay out a steel panel which will be used to shield the operator from the hazard of a steel reaction vessel operating at 5,000 psi. The vessel has a capacity of 1 qt.

The panel is to be equipped with five high-pressure valves, two Bourdon pressure gauges, a temperature indicator, and five electric switches.

4-3. Plan a high-pressure cell for experimental work on a chemical reaction of somewhat uncertain nature. If the vessel should burst, a volatile, flammable liquid would be released in the room. The vessel has a capacity of 5 gal and will operate under pressures up to 5,000 psi. Indicate a complete system for protecting the vessel and the operating personnel.

4-4. Make a list of 10 possible hazards involved in operating high-pressure equipment.

4-5. A vessel containing propane as a liquid under pressure is stored in a room 10 by 15 by 9 ft. Calculate the minimum weight of propane which, if it escapes into the room, would permit a flammable mixture to exist throughout the whole room.

4-6. A high-pressure plant for the synthesis of methanol is under construction, and you are to be in charge of the operating personnel. Outline a program of instruction and training for the operators who are to be recruited from the local labor market.

Chapter 5

5-1. Calculate the work of compression when gaseous propane is compressed isentropically from 80°F and 60 psi to 300 psi.

5-2. Calculate the isentropic work of compression when ethane is compressed from 0°F and 100 psi to 800 psi. Repeat for an initial temperature of 100°F.

5-3. Ethane is to be compressed from 80°F and 14.7 psi to 500 psi in two isentropic stages without clearance and with intercooling. Construct a suitable chart of volume vs. temperature as shown in Fig. 5-46 for ethane, and using the graphical method calculate the interstage pressure which will require the least work of compression. Determine the work of compression per pound of ethane.¹

Chapter 6

6-1. Make a graph similar to that shown in Fig. 6-2 for the wall of a cylindrical vessel 2 in. ID by 4 in. OD constructed of AISI A4340 steel when the vessel is under an internal pressure of 30,000 psi. What is the value of the elastic-breakdown pressure? See Table 6-3 for σ_y .

6-2. The vessel described in Prob. 6-1 is heated under steady-state conditions so that the outer wall is at 250°F and the inner wall is at 50°F. Determine the tangential-stress distribution due to the combination of the internal pressure of 30,000 psi and the temperature gradient. Calculate the elastic-breakdown pressure while the vessel is being heated.

6-3. A cylinder is to be reinforced by winding with wire. Using the same allowable stresses as those described by Comstock in the text, determine the values of K_1 and K_2 when the specified internal pressure p'_1 is 20,000 psi. Calculate the tension σ_w in the wire during application at several values of K .

6-4. A cylindrical vessel is to be constructed of SAE 3320 steel with a ratio of outside to inside radius of 2.5. Calculate the elastic-breakdown pressure, the over-strain pressure, and the bursting pressure. The steel is initially under no residual stress.

6-5. Design a vessel to withstand an internal pressure of 3,000 atm. The internal volume is to be approximately 20 cu in. The vessel will be used at temperatures as

¹ The properties of ethane may be found in J. H. Perry, editor, "Chemical Engineers' Handbook," 3d ed., pp. 257-258, McGraw-Hill Book Company, Inc., New York, 1950.

high as 500°F and will contain compressed hydrocarbon gases but not hydrogen. Select the material of construction for the vessel walls, determine the internal and external diameters and the length, and choose the general type of closure. Repeat for use with gases containing appreciable hydrogen.

6-6. Show that Eq. (6-62) follows from Eq. (6-61) under the conditions specified in the text.

6-7. Show that Eq. (6-60) may be derived from Eq. (6-47) under the conditions specified in the text.

6-8. Cylinder 6 in Tables 6-3 and 6-4 with a residual circumferential stress at the bore of 26,000 psi had an observed overstrain pressure of 111,000 psi. Calculate the overstrain pressure for this vessel, and compare with the observed value.

6-9. It has been proposed that the external pressure required to collapse the wall of a long cylinder with $K > 1.1$ may be calculated from the formula

$$\frac{\sigma_y}{p_c} = \frac{2}{1 - 1/K^2}$$

where σ_y is the stress at the yield point and p_c is the collapsing pressure. Show that this formula follows from the Lamé equations if collapse occurs when the maximum compressive stress is equal to that at the yield point and if p_1 is zero.²

6-10. A tube 0.5 in. OD and 0.35 in. ID is made of a steel with tensile and compressive yield strengths of 50,000 psi. If the steel is not to be stressed beyond elastic breakdown, calculate (a) the maximum external pressure which can be applied with atmospheric pressure on the inside, and (b) the maximum internal pressure that could be applied if the external pressure determined in (a) were also applied. (c) Make a plot of σ_t/p_1 when $p_2 = 0$ and $K = 3$.

6-11. Calculate the distribution of stresses σ_t , σ_r , σ_z throughout the wall of a cylinder where $K = 2$ when subjected to the overstrain pressure on the inside. Now determine the stress distribution throughout the wall after this pressure has been released. Compare the results with Figs. 6-10 and 6-11.

Chapter 7

7-1. Prepare an outline showing several of the chief problems involved in the determination of each of the following properties at high pressure: (a) pVT properties, (b) phase equilibrium, (c) heat capacity, (d) viscosity, (e) thermal conductivity.

Chapter 8

8-1. Calculate the volume of 1 lb mole of hydrogen at 100°C and 100 atm using the van der Waals equation, the Beattie-Bridgeman equation and the measured values of pV .

8-2. Calculate the volume of 1 g mole of carbon monoxide at 100°C and 1,000 atm using the Redlich and Kwong equation, the van der Waals equation, and the measured values of pV .

8-3. Calculate the volume of 1 lb mole of ethylene at 100°C and 1,000 atm using the van der Waals equation, the Benedict-Webb-Rubin equation, and the measured values of pV .

8-4. Evaluate the following properties of ethylene at 100°F and 300 atm: (a) density, lbs/cu ft, (b) heat capacity, Btu/(lb)(°F), (c) enthalpy, Btu/lb, (d) thermal conductivity, Btu/(hr)(ft)(°F), (e) fugacity, atm. At 1 atm and 100°F the properties

² See T. M. Jasper and J. W. W. Sullivan, The Collapsing Strength of Steel Tubes, *Trans. ASME*, **53**(17b):219 (1931).

of ethylene are heat capacity 9.85 Btu/(lb mole)(°F), enthalpy 130 Btu/lb, and thermal conductivity 0.0126 Btu/(hr)(ft)(°F).

8-5. Ethylene is to be stored in a cylinder with a capacity of 2 cu ft. Calculate the weight of ethylene in the cylinder when under a pressure of 2,000 psia and a temperature of 80°F. What weight would be predicted by the perfect-gas laws? Compare the answer obtained by using the compressibility-factor charts, Figs. 8-7 to 8-9, with that from Table D-4.

8-6. Using Table D-4, calculate the compressibility factor for ethylene at 25°C over the range of pressures from 0 to 600 atm. Make a plot of the percentage deviation from the experimental values of $z = pv/RT$ as calculated by the perfect-gas law and also by Figs. 8-7 to 8-9.

8-7. Calculate the viscosity and thermal conductivity of carbon dioxide, ethylene, and methane at 150 atm abs and 40°C. The properties at 1 atm and 40°C are as follows:³

Compound	μ_1 centipoises	k_1 (Btu)(ft)/(hr)(sq ft)(°F)
Carbon dioxide.....	0.0150	0.0104
Ethylene.....	0.0105	0.0125
Methane.....	0.0110	0.0201

8-8. The pV values for ethylene are given in Table D-4. Using the method of residuals and a graphical procedure, calculate the effect of pressure on the enthalpy of ethylene at 75°C for the pressure range 1 to 2,000 atm. Note that

$$\alpha = \frac{RT}{p} - v$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} - \left(\frac{\partial \alpha}{\partial T}\right)_p$$

$$\Delta H = \int_0^p dH = \int_0^p \left[v - T \left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

according to Eq. (8-62), where ΔH is the isothermal change in enthalpy from zero pressure to the pressure p .

Amagat units for pV are defined so that the product of pressure and volume is unity at 1 atm abs and 0°C. The symbol pV used in tables of Amagat units may be interpreted as $pV/p_s V_s$, where p_s is 1 atm and V_s is the volume at 1 atm and 0°C.⁴

8-9. The values of pV in Amagat units (see Prob. 8-8) for hydrogen are given in Table D-1. Hydrogen has a molal volume of 22,428 cu cm/g mole at 1 atm and 0°C. Using this data and a graphical method employing residuals, calculate the heat capacity at constant pressure of hydrogen at 50°C from 0 to 2,000 atm. The heat capacity at constant pressure at 1 atm and 50°C is 6.88 cal/(°C)(g mole).

8-10. Methanol is forced into a vessel where the pressure is 400 atm at 20°C using a piston-and-cylinder arrangement. Calculate the percentage change in volume of the methanol when the pressure on it is increased from 1 to 400 atm at constant temperature.

³ From Perry, *op. cit.*

⁴ For values of the molal volume of gases at 1 atm and 0°C, see Perry, *ibid.*, p. 205. This value for ethylene is 22,240 cu cm/g mole. The enthalpy should be expressed in calories per gram mole in this problem.

COMPRESSIBILITY FACTORS FOR NITROGEN-ETHYLENE MIXTURES AT 50.07°C†

Pressure, atm.	z, 19.8% N ₂	Pressure, atm.	z, 40.1% N ₂	Pressure, atm.	z, 59.7% N ₂	Pressure, atm.	z, 79.6% N ₂
1.197	0.9961	4.104	0.9912	1.213	0.9985	1.245	0.9993
4.037	0.9868	5.223	0.9888	3.990	0.9951	3.948	0.9978
9.491	0.9689	10.176	0.9782	5.346	0.9934	10.249	0.9945
10.131	0.9668	10.275	0.9780	9.736	0.9882	10.799	0.9942
11.622	0.9618	11.694	0.9750	10.463	0.9873	12.441	0.9934
13.538	0.9554	13.656	0.9708	12.041	0.9854	14.575	0.9924
16.588	0.9453	16.797	0.9642	14.086	0.9830	17.365	0.9910
17.092	0.9436	17.646	0.9624	17.379	0.9792	18.022	0.9907
18.527	0.9387	18.809	0.9600	17.389	0.9792	20.249	0.9897
20.082	0.9335	20.430	0.9566	19.498	0.9768	22.053	0.9889
31.872	0.8935	23.241	0.9507	21.202	0.9749	23.725	0.9882
36.147	0.8789	33.569	0.9296	22.408	0.9736	33.962	0.9842
37.868	0.8730	38.311	0.9202	33.626	0.9615	39.089	0.9824
41.504	0.8605	42.434	0.9121	38.568	0.9564	44.749	0.9806
49.720	0.8324	44.352	0.9084	41.600	0.9534	45.744	0.9803
54.766	0.8152	53.851	0.8905	44.936	0.9502	56.498	0.9776
58.719	0.8019	59.836	0.8797	55.115	0.9410	63.456	0.9763
66.349	0.7767	64.611	0.8715	61.631	0.9356	69.106	0.9754
74.089	0.7523	77.911	0.8503	66.885	0.9315	87.537	0.9740
83.652	0.7243	88.305	0.8358	79.312	0.9230	100.97	0.9744
98.464	0.6884	90.216	0.8334	90.811	0.9165	103.61	0.9746
107.70	0.6695	101.53	0.8195	93.294	0.9153	118.67	0.9765
139.29	0.6411	122.92	0.8010	105.77	0.9103	148.12	0.9841
162.61	0.6490	137.23	0.7952	130.19	0.9047	167.87	0.9917
203.61	0.6930	149.23	0.7933	146.44	0.9060	184.64	1.0007
322.86	0.8873	169.88	0.7968	160.11	0.9075	213.62	1.0202
467.86	1.1433	200.48	0.8156	184.16	0.9174	254.20	1.0529
.....	249.71	0.8663	217.13	0.9381	314.48	1.1108
.....	370.62	1.0381	267.10	0.9840	439.40	1.2532
.....	495.80	1.2347	374.15	1.1130	546.96	1.3868
.....	640.96	1.4644	470.70	1.2449	655.74	1.5255
.....	572.64	1.3894

† From W. P. Hagenbach and E. W. Comings, *Ind. Eng. Chem.*, **45**:606 (1953).

8-11. Calculate the fugacity coefficients for a mixture of 66 mole per cent hydrogen and 34 mole per cent carbon monoxide making use of the generalized charts. The mixture is at 100°C and 1,000 atm.

8-12. Repeat the calculation of the fugacity coefficient under the conditions of Prob. 8-11 using Eq. (8-136) and the equations that follow it.

8-13. A mixture of 80 mole per cent ethylene and 20 mole per cent methane is to be heated from 80 to 200°F while under a pressure of 1,500 psia. Estimate the heat which must be added under steady-state-flow conditions per pound mole of mixture. For these vapors at 1 atm,

$$\begin{aligned}
 C_p &= 3.42 + 9.91 \times 10^{-3}T + 1.28 \times 10^{-2}T^6 && \text{for } \text{CH}_4 \\
 C_p &= 2.71 + 16.20 \times 10^{-3}T + 2.80 \times 10^{-6}T^2 && \text{for } \text{C}_2\text{H}_4
 \end{aligned}$$

where T = temperature, $^{\circ}\text{R}$
 C_p = Btu/(lb mole)($^{\circ}\text{R}$).

8-14. Derive an expression for the fugacity of a pure gas which is represented by the van der Waals equation. Consider only a change in pressure at constant temperature, and express the fugacity as a function of either p or v .

8-15. The data obtained by Hagenbach on the compressibility coefficients of nitrogen-ethylene mixtures at 50°C are tabulated on page 531. Calculate the fugacity of each component in any one of the four compositions you wish to select over the range of pressure covered by the data. Compare the calculated values with those predicted by the Lewis and Randall Fugacity rule.

8-16. A mixture of 80 mole per cent ethylene and 20 mole per cent methane is to be stored in a cylinder with a capacity of 2 cu ft. Calculate the weight of the mixture when the storage pressure is 1,500 psia at 80°F . Compare with the value predicted by the perfect-gas law.

8-17. Calculate the volume required to hold 100 lb of a 50 weight per cent mixture of propane and n -butane at 100 atm abs and 175°C . Compare the values calculated by using (a) Amagat's law, (b) the pseudocritical method.

8-18. Repeat the calculations for the fugacity of nitrogen and the fugacity of ethylene in the mixture of the composition chosen in Prob. 8-15, using Eq. (8-136). Compare the results with the values calculated from experimental pVT measurements.

8-19. Determine the value of B in Eq. (8-161) for the system toluene- n -hexane at a single temperature. C and D are zero. Refer to the literature for the necessary information.

8-20. The vapor-liquid equilibrium for the system toluene- n -hexane is shown in Fig. 9-7. Calculate the adjusted vapor pressure and γ'_i for both components at one point on the curve for 350 psi. Test your results, using Eq. (8-175).

Chapter 9

9-1. A mixture of 80 mole per cent ethylene and 20 mole per cent methane is to flow through 100 ft of 0.25-in. = ID tubing at a velocity of 15 ft/sec and under an average pressure of 150 atm at a temperature of 80°F . Calculate the rate of flow in pounds per minute and the pressure drop along the tube. The viscosity of the mixture under these conditions is estimated to be 0.028 centipoise.

9-2. Ethylene is flowing through a 1-in.-ID tube at a rate of 8,480 lb/hr. The average temperature is 70°F , and the pressure is 100 atm. Under these conditions the heat-transfer coefficient h for transfer between the ethylene and the tube wall has been calculated and found to be 8150 Btu/(hr)(sq ft)($^{\circ}\text{F}$). If this same rate of flow and temperature is maintained but the pressure is increased to 200 atm, calculate the heat-transfer coefficient.

9-3. Carbon dioxide is confined between two parallel steel walls at a pressure of 120 atm. One wall is at 95°F and the other is at 120°F . If the walls are at first 0.002 in. apart and are progressively moved further apart, at what distance will convection currents begin to appear in the gas layer?

9-4. A mixture of 1.5 mole per cent acetone in air is to be stripped by absorbing 99 per cent of the acetone in water in a tower packed with 1-in. Berl saddles. The average temperature of both gas and water is 60°F . Compare the height of the tower required when the total pressure is 185 psig with that required when it is 0 psig. The water rate is 4,000 lb/(hr)(sq ft) and the gas rate is 200 lb/(hr)(sq ft). The liquid-film resistance is small and may be neglected for this calculation. The Henry's-law constant H for the vapor pressure of acetone over dilute aqueous solutions in the temperature range of 15 to 45°C is given by Zabban and Dodge as

$$\log H = \frac{2,125}{T} - 6.9525$$

where T = temperature, °K

H = ratio of concentration in the liquid to partial pressure in the gas, lb mole/(cu ft)(atm)

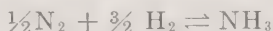
9-5. What is the maximum rate of heat transfer that can be obtained in the boiling of ethanol from a clean surface? State also the temperature, total pressure, and the temperature difference across the boiling film when this rate is attained.

9-6. A heater is to be designed to heat ethylene under a constant pressure of 100 atm from 70 to 200°F. The ethylene will flow through 1-in.-ID tubes heated by condensing steam. The inner surface of the tubes will be maintained at an essentially constant temperature of 220°F. If the velocity at the inlet to the heater is 20 ft/sec, calculate the length of tube required.

9-7. Nitrogen gas at 100°F and 500 atm is to flow through a 1-in.-ID straight tube. Considering the gas as incompressible under these conditions, make a plot of the pressure drop per 100 ft of tube vs. the velocity, with the latter covering a range up to 30 ft/sec. Repeat for 100 atm; 1,000 atm.

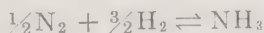
Chapter 10

10-1. Calculate the per cent ammonia and per cent conversion at equilibrium at 300 atm and 700°K resulting from a mixture of the following initial composition: 68 mole per cent N_2 , 22 mole per cent H_2 , 10 mole per cent CH_4 . Under these conditions $K = 0.0091$, and $K_\phi = 0.72$ for the reaction



10-2. Consider an ideal (and reversible) process in which pure nitrogen gas and pure hydrogen gas at atmospheric pressure and 100°F enter a reaction system in the molal ratio of 1:3. This system may contain gas compressors, heat exchangers, gas-expansion engines, and the like. Pure ammonia gas at atmospheric pressure and 100°F is removed from the system. What is the minimum amount of work which must be done by the surroundings on this system if the chemical reaction takes place at 100°F and 1 atm; at 300°F and 200 atm?

10-3. A mixture of 80 mole per cent hydrogen and 20 mole per cent nitrogen reacts to form ammonia at 300°C and 200 atm. Calculate the per cent conversion at equilibrium. At this temperature $K = 0.063$ for the reaction



10-4. If the methanol reaction were carried out with a mixture consisting of 1 mole of hydrogen to 1 mole of carbon monoxide, calculate the mole per cent methanol in the mixture when equilibrium is attained at 300°C and at 100, 200, and 500 atm. The value of K is 2.316×10^{-4} at 300°C for the reaction



10-5. The synthetic ammonia process is normally operated by recycling the unconverted N_2 - H_2 mixture to the converter. If the 1:3 molal mixture entering the reactor contains 10 mole per cent methane and reaches equilibrium at 400°C and 200 atm, calculate the equilibrium degree of completion.

10-6. Calculate the composition of the equilibrium mixture which results from a mixture of 3 moles of hydrogen and 1 mole of nitrogen at 500°C and 1,000 atm. Compare the answers obtained by using Joffe's method with that from the Redlich and Kwong equation.

Chapter 11

11-1. Carry out the integration of Eq. (11-21) for a reaction which proceeds significantly only in the forward direction as shown by Eq. (11-2). Let $a = 1$, $b = 0$, and $c = 0$.

11-2. Repeat Prob. 11-1 for the case where $a = 2$, $b = 0$, and $c = 0$; and for $a = 1$, $b = 1$, and $c = 0$.

11-3. The substance A decomposes by a first-order reaction. Substances B and C react in a separate vessel according to a second-order reaction. These are both homogeneous gas-phase reactions. Neglecting any reverse reactions, make a plot of the moles of A vs. time. Do the same for the moles of B plus C vs. time on the same graph. There is 1 lb mole of A initially and 1 lb mole of B plus C initially, and in each case this is reduced to $\frac{1}{2}$ mole in 1 hr. The reactions take place at constant pressure. State any additional assumptions you make.

Chapter 12

12-1. Prepare a set of curves similar to those in Figs. 12-23 and 12-24 for 3 moles of hydrogen to 1 mole of nitrogen at 300 atm, using the rate of ammonia formation from the curves in the text.

12-2. It is proposed to make 10 million lb/year of methanol from carbon monoxide and hydrogen derived from natural gas (consider this to be 100 per cent methane). Discuss in a few lines the choice of the other necessary reactants. Choose one combination of reactants, and estimate roughly as best you can (a) the methane required in cubic feet per minute, (b) other reactants in cubic feet per minute, (c) the size of converters (or rather volume of catalyst) required.

12-3. The reaction $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ is taking place in a catalyst bed. N_0 is the moles of reaction mixture (CH_3OH -free) entering the reactor in unit time, and Z is the mole per cent CH_3OH in the mixture at any section through the catalyst bed (normal to the direction of flow). $N_{\text{CH}_3\text{OH}}$ is the moles of CH_3OH per N_0 moles entering for any section of the bed.

a. Express $dN_{\text{CH}_3\text{OH}}/dx$ in terms of dZ/dx , Z , and N_0 , where x is distance through the reactor.

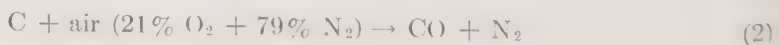
b. If this catalyst bed is cylindrical, show graphically by a freehand sketch how you would expect temperature and Z to change with distance along a radius at two sections of the reactor. The reactor walls are cooled, and the temperature along the axis may be considered constant.

12-4. In Fig. 12-3 the amount of ammonia in the exit gas from a small ammonia-synthesis catalytic converter is 10.1 per cent when the space velocity is $50,000 \text{ hr}^{-1}$. The converter is operated essentially isothermally at 300 atm and 500°C using a mixture of 3 moles of hydrogen to 1 mole of nitrogen. Carry out the integration of Eq. (12-47) graphically for these conditions, and determine the value of the constant f' . Compare the result with that in Table 12-4.

12-5. One method of preparing a mixture of 25 mole per cent N_2 , 75 mole per cent H_2 is to treat coke with steam in a water-gas converter.



This is mixed with the proper amount of producer gas,



and the mixture passes through a shift converter in which the CO is converted to

CO₂ and additional H₂ is formed,



The gas is then compressed to 25 atm, and the CO₂ is scrubbed out with water. If each of these reactions is completed and no impurities are present, calculate the saving in energy for compression per 100 lb moles of final mixture (express as horsepower-hours) (a) if all three reactions are carried out at 25 atm instead of at 1 atm followed by compression to 25 atm; (b) if reactions (1) and (2) are at 1 atm, and (3) at 25 atm. Assume isothermal compression of the gas at 70°F. Water may be introduced as liquid and then vaporized without compression of the vapor.

12-6. A plant is to be designed for installation in a Texas city to produce 100,000 tons/year (300 operating days of 24 hr each). The flow diagram is shown in Fig. 12-6.

a. Estimate the rate of consumption of natural gas (90 per cent CH₄ and 10 per cent N₂) in cubic feet per hour (measured at 60°F and 1 atm) if all the CH₄ is converted to CO + H₂. The purge gas amounts to 5 per cent of the make-up gas leaving the final compressor. All ammonia is eventually recovered as product.

b. If the space velocity in the converter, based on the entering gas, is 100,000 hr⁻¹, estimate the total volume of catalyst required. The gas entering the converter contains 8 per cent inerts, 3 per cent NH₃, and the rest is a 3:1 H₂-N₂ mixture.

c. What percentage of the equilibrium composition (per cent NH₃) based on pure 3:1 H₂-N₂ mixture is reached in the reactor?

GLOSSARY

Activation. A physical or chemical change in an intended catalyst which transforms it to a form in which it has catalytic properties.

Activity. A relative fugacity or a relative effective concentration. The activity is evaluated according to thermodynamic principles and thus follows equilibrium relationships rigorously while pressure and concentration do not [see Eq. (8-56)].

Activity Coefficient. The ratio of the activity of a component in a mixture to its mole fraction [see Eqs. (8-141) and (8-142)].

Adiabatic. A term applied to a change or process in which heat does not enter or leave the system except as part of the energy of streams of matter which enter or leave.

Alkylation. The addition or substitution of an alkyl group: for example, a reaction in which paraffin hydrocarbons combine with olefins.

Amagat, Units of. A system of units in which pressure, volume, density, pV , and the like are each given values relative to unity at 0°C and 1 atm.

Amination. The chemical process of preparing a compound containing an $-\text{NH}_2$ group united to a radical other than an acidic radical.

Ammonolysis. A process analogous to hydrolysis but involving ammonia instead of water: for example, the addition of an $-\text{NH}_2$ group to one part of a molecule and a hydrogen atom to another part, breaking the original compound into two new compounds.

Annealing. The process of heating a metal, glass, or other substance above a definite temperature and then cooling it slowly. This usually modifies its properties, relieves strains, and decreases brittleness.

Autoclave. A pressure vessel equipped for heating (and frequently agitating) the contents.

Autofrettage. A process for strengthening the walls of a pressure vessel by applying a pressure to the inside until the walls yield in plastic flow to some extent. This pressure is relieved, the vessel is given a stress-relieving anneal, and the process is repeated. Finally the inner wall fibers are under compression and the outer fibers under tension when no pressure is applied to the inside. This is a favorable stress distribution.

Autothermic Reaction. A chemical reaction carried out above the ambient temperature where only the heat of reaction is used to raise the temperature of the reactants to the reaction temperature.

Batch Operation. An operation or process carried out in a cycle such as the introduction of a mixture to a vessel, followed by heating, cooling, and discharging. This may be compared to a continuous operation where the process is not cyclic.

Beckmann Thermometer. A mercury-in-glass thermometer constructed to measure small changes in temperature of the order 0.001°C and greater.

Blue Water Gas. The gas produced by the action of steam on incandescent coke. Composition varies, but a typical analysis is 45.5 per cent CO , 45 per cent H_2 , 4 per cent CO_2 , 1.5 per cent O_2 , 2 per cent CH_4 and CH_3CH_3 , and 2 per cent N_2 .

Booster Compressor. A compressor used to raise the pressure of a gas over a small range at an elevated pressure: for example, in order to recycle gases from a reactor through a product-recovery train and back to the feed stream.

Border Curve. The curve that represents a relation between the pressure and temperature where a volatile mixture begins to change from a liquid to a vapor or from a vapor to a liquid.

Boundary Conditions. A term used in mathematics to denote the conditions defined by a given case or application and used in determining the constants which result from the solution of differential equations.

Boyle Point. The temperature of an actual gas where it most closely obeys Boyle's law. Above this temperature throttling results in a rise in temperature; below this temperature, throttling results in a decrease in temperature.

Break In. To operate a bearing, packing gland, or other device to cause enough wear so that it performs as intended.

Bubble Point. The combination of temperature and pressure at which a volatile liquid produces the first bubble of vapor in equilibrium with the liquid.

Calorimeter. An instrument for measuring the amount of heat produced in a process, such as in the combustion of a fuel, or the amount of heat added to a system or removed from it by heating or cooling.

Carbonylation. The addition of a carbonyl group as in the OXO process.

Catalytic Polymerization. A polymerization reaction brought about by a catalyst rather than by temperature or pressure alone.

Catalytic Water Gas. The gas produced when carbon monoxide and steam react in the presence of a catalyst (an endothermic reaction). The reaction is also called the water-gas-conversion reaction or the shift reaction. A typical analysis of the gas is 65 per cent H_2 , 30 per cent CO_2 , 2 per cent CO , and 3 per cent N_2 and inert gases.

Cathetometer. An instrument for the accurate measurement of differences in position; one type of instrument measures differences in height, another differences in horizontal position.

Charging Stock. A mixture fed to a process such as the mixture of petroleum hydrocarbons fed to a cracking unit.

Chemical-reaction Kinetics. The quantitative interpretation and formulation of the rates of chemical reactions in contrast to chemical equilibrium.

Chromel-Alumel. An alloy of 90 per cent nickel and 10 per cent chromium (Chromel P) and one of 94 per cent nickel, 3 per cent manganese, 2 per cent aluminum and 1 per cent silicon (Alumel) used for thermocouples up to $1300^{\circ}C$.

Chu. The quantity of heat which causes the temperature of 1 lb of water to increase $1^{\circ}C$.

Coke-oven Gas. The gas from coke ovens in which the destructive distillation of coal is carried out. A typical composition is 53 per cent H_2 , 31.6 per cent CH_4 , 3.4 per cent N_2 , 6.3 per cent CO , 1.8 per cent CO_2 , 0.2 per cent O_2 , 3.7 per cent illuminants.

Commercial Feasibility. The assurance that a process can be financed and operated at a profit in competition with other processes.

Component. One of the ingredients in a mixture. The term component as used in Gibbs' phase rule implies that the minimum number of elements or compounds from which the mixture can be prepared will be used. For example, a mixture of H_2 , O_2 , and H_2O could be prepared from any two of these ingredients. When chemical equilibrium exists between these three ingredients, they comprise a system of two components. When no chemical reaction takes place, the system comprises three components.

Compressibility, Gases. The deviation from Boyle's law or the perfect-gas law as represented by compressibility factors variously defined.

Compressibility, Liquids. The fractional rate of change in volume with pressure,

$$\frac{1}{V} \frac{dV}{dp} \text{ or } \frac{1}{V_0} \frac{dV}{dp}$$

Compressibility Factor. The product pV measured in units such that $pV = 1.0000$ at 1 atm and 0°C ; or it may be defined as $z = pv/RT$, where $z = 1.0000$ as p approaches zero. These are not the same.

Consecutive Reactions. Reactions involving the product of a reaction with its reactants or products.

Constantan. An alloy of 60 per cent copper and 40 per cent nickel used for thermocouple wire.

Conversion. When applied to a chemical reaction, the extent to which the reaction takes place. The fractional conversion is the fraction of the limiting reactant which has reacted.

Converter. The vessel or container in which a chemical reaction takes place.

Crank End. The end of a compressor toward the crank. A gas compressor consists of pistons in cylinders closed at one end by a solid head and at the other end by a head which contains an opening for the piston rod. The piston rod is driven by a crankshaft.

Creep. The slow elongation of a metal when subjected to a continuous stress at elevated temperatures above about 700 or 800°F (see Sec. 3-5).

Cricodentherm. The maximum temperature of a mixture of definite composition which permits a gas and a liquid phase to exist in equilibrium. This temperature differs from the critical temperature and also from the temperature corresponding to the maximum pressure which permits the coexistence of gas and liquid phases.

Critical Pressure. The pressure where the gas and liquid phases have the same density. This applies to a pure substance or to a mixture of a definite composition.

Critical Temperature. The temperature where the gas and liquid phases have the same density. This applies to a pure substance or to a mixture of a definite composition.

Degree of Completion. The extent to which a chemical reaction proceeds to completion. The fraction of the limiting reactant which undergoes reaction. The same as fractional conversion.

Dehydrant. A substance which removes or absorbs water and renders it unavailable to other components in the system.

Dehydrogenation. A reaction that results in a reduction in the hydrogen content of a substance.

Dehydrohalogenation. The removal of a hydrogen and a halogen atom such as HCl from an organic halide.

Dewar Flask. A double-walled vessel with the space between the walls evacuated to prevent the conduction and convection of heat. When made of glass, the walls are silvered to reduce radiant-heat transfer.

Dew Point. The combination of temperature and pressure at which a condensible vapor produces the first small amount of liquid in equilibrium with the vapor.

Diffusivity. The diffusion coefficient or proportionality constant relating a concentration gradient to the time rate of change of concentration at a point in a quiescent mixture.

Dimensions. The kinds of quantities for which primary units are defined (see Appendix A).

Double-acting. A term applied to a compressor in which fluid is compressed or pumped during both the forward and backward travel of the piston. When the stroke is effective only during travel in one direction, it is termed single-acting.

Doubly Promoted Catalyst. A catalyst which contains two noncatalytic substances which enhance or promote the activity of the catalyst. For example, the catalyst for the synthesis of ammonia is iron promoted with potassium oxide and aluminum oxide.

Drag. The force exerted on a body by a fluid flowing over its surface.

Duplex Pump. A pump having two cylinders operated in parallel to provide a more continuous flow of liquid.

Economic Analysis. The determination or prediction of costs, market trends, profits, and the like for proposed or existing process designs.

Economizer. A boiler or heat exchanger used to recover the heat developed by a chemical reaction from the gaseous products.

Elastically. A term used for behavior such that a substance resists deformation by a force and returns to its original form when the force is removed.

Elastic Behavior. The nature of the distortion and its quantitative relation to the forces which caused it when a body is deformed elastically.

Energy of Activation. The energy in excess of an average state which must be acquired by molecules in order to undergo a particular reaction.

Enthalpy. The sum of internal energy and the product of the pressure and the volume. Thus $H = E + pv$. This is a state property of a substance or mixture and has a single value for each set of specified conditions.

Entropy. A state property of a substance or mixture which has a single value for each set of specified conditions. This value is determined by evaluating the integral $\int dq/T$ from a reference state to the state determined by the specified conditions along any arbitrary reversible path.

Envelope Curves and Surfaces. A two- or three-dimensional model of the ranges of temperatures, pressures, and compositions of a mixture in which a liquid and vapor exist in equilibrium. The boundary of this region is called an envelope. A curve passing through points on the envelope is called an envelope curve.

Equilibrium composition. The composition of a mixture after the components have reached chemical equilibrium under specified conditions such as temperature and pressure.

Esterification. The chemical reaction which forms an ester: for example, by joining an acid and an alcohol with the removal of water.

Eutectoid. In a temperature-composition diagram representing the phase equilibrium between a solid solution and the solid components, the material of the composition at the minimum (eutectoid) temperature (see Sec. 3-3).

Expansion Valve. A valve used to lower the pressure of a fluid.

°Fep. Degrees Fahrenheit end-point temperature in a distillation.

Film Coefficient. The proportionality constant relating the temperature or concentration difference across a thin layer or film at a fluid-solid surface to the rate of transfer per unit area. The chief resistance to the transfer of heat or matter from a fluid to a solid surface often lies in this thin layer next to the surface.

Flash Chamber. The space provided for the associated change in volume when the pressure of a hot, volatile liquid is suddenly decreased and part of it flashes to vapor.

Flash Point. The minimum temperature of a liquid required to produce sufficient vapor in the region above it to ignite when a flame is passed over the liquid. This is an important test of lubricating oils, solvents, and other liquids.

Flow Sheet. A chart or diagram which shows the related steps of a process in the sequence in which they take place.

Free Energy. A property of a pure substance or a mixture defined as follows,

$$F = E + pv - TS$$

The change in free energy represents the energy which must be added as work or may be obtained as work when a process takes place reversibly at constant temperature and pressure.

Friedel-Craft Reaction. The type of reaction which employs anhydrous aluminum chloride to bring about the synthesis of aromatic hydrocarbon derivatives in a mixture of components such as an aromatic and an alkyl halide.

Fugacity. A quantity which replaces pressure or partial pressure and thus permits the calculation of the isothermal work of compression for a real gas by using the equation for a perfect gas (see Sec. 8-5).

Fugacity Coefficient. The ratio of the fugacity of a pure substance to its pressure (see Sec. 8-5). For a definition of the fugacity coefficient for a component in a mixture see Sec. 8-15.

Galling. The condition that metal parts, when rubbing together, create excessive friction, or the surfaces seize together such as when male and female threads bind.

Galvanometer. An electric instrument for measuring or detecting a small current. It may be designed to be sensitive to the voltage impressed across it.

Gas-film Absorption Coefficient. See **Film Coefficient.** The film coefficient that applies to the gas film adjacent to a gas-liquid interface when absorbing a component of a gas mixture.

Geometric Mean. The n th root of the product of n positive values.

Gerbitol System. A process for removing acid gases such as hydrogen sulfide and carbon dioxide by absorption in ethanolamines.

Gradient. The rate of change of a property or condition with distance in an indicated direction and at a point.

Halogenation. A reaction in which a halogen is added to or substituted in an organic compound.

Head End. The end toward the solid head. See **Crank End.**

Heat Capacity. The amount of heat which will cause the temperature of a specified mass of matter to increase one degree in temperature. The temperature may be in degrees Fahrenheit or Centigrade, and the mass of matter in pounds, grams, pound moles, or gram moles. When expressed as Btu/(lb)(°F), cal/(g)(°C), or Chu/(lb)(°C), the numerical values are the same.

Height of Transfer Unit. Approximately the height of a packed column such that the change in composition of a component in (or of the temperature of) the mixture flowing through it is equal to the average driving force throughout this height.

Heterogeneous Reaction. A term which usually refers to a chemical reaction which takes place wholly or partly on a solid surface such as on a solid catalyst. In general, a chemical reaction in which more than one phase is involved.

Hot Point. The region which usually occurs in an exothermic reaction in a catalyst bed part of the way through the bed where the temperature has a maximum value.

Hydroammonolysis. A reaction in the presence of ammonia, hydrogen, and a catalyst in which both reagents take part with amines as products.

Hydroforming. A process used in petroleum refining to improve the octane number and other properties of a hydrocarbon mixture. The process operates in the ranges of 480 to 540°C and 150 to 300 psi and uses a catalyst in the presence of hydrogen gas to bring about cracking and other reactions with a minimum of carbon formation.

Hydroformylation (OXO Reaction). The treatment of olefins with hydrogen and carbon monoxide with a cobalt catalyst at elevated temperature and pressure to produce aldehydes with one carbon atom added to the starting compound.

Hydrogenation. A reaction in which hydrogen combines with another compound such as in the hydrogenation of vegetable oils which contain unsaturated double bonds.

Hydrogenolysis. The splitting of a molecule on the addition of hydrogen.

Hydrolysis. A reaction in which one compound combines with the hydrogen from water and another with the hydroxyl group. The water molecule is split, and the products of the reaction may result from the splitting of another molecule.

Hysteresis. The effect of a sort of internal friction in a body. When deformed according to one relation between stress and strain, it recovers according to a different relation, thus showing a loop on a graph of its behavior (see Fig. 5-7).

Ideal Gas. See **Perfect Gas**.

Ideal Solution. A mixture whose components show no interaction. The pure-component volumes are additive at any pressure up to the pressure of the mixture, and there is no heat of mixing. An ideal liquid solution behaves at all temperatures and compositions according to Raoult's law.

Inert Gas. One that will not react chemically under the conditions prevailing in a process.

Intensifier. A double cylinder with a large-diameter piston directly connected to a piston of small diameter. A fluid at low pressure acts on the large piston, and the small piston exerts a greater pressure on another body of fluid. See Fig. 5-40.

Intensive Property. A property, such as energy per unit mass or volume per unit mass, which does not depend on the size or mass of material in a system.

Intermolecular Forces. The force which is exerted upon a molecule by those molecules which are near it. A perfect gas is one in which the molecules act independently. When real molecules are crowded closer together as by an increase in pressure, the intermolecular forces increase.

Isentropic. A change, or path, or its mathematical representation in which the entropy has a constant value. When a change is adiabatic, it is also isentropic if it is carried out reversibly.

Isobar. A path or curve on a graph or a mathematical expression such that the pressure has a constant value.

Isomate Process. A method of converting low-octane pentanes and hexanes into isomers of higher octane number. A slurry of hydrocarbon-aluminum chloride complex is used as a catalyst with anhydrous HCl and hydrogen in the range of 240 to 250°F and 700 to 800 psi.

Isomerization. A process for rearranging a normal compound to form isomers. For example, catalytic isomerization of *n*-butane is carried out in the petroleum industry.

Isometric. A path or curve or its mathematical expression such that the volume is constant for the system.

Isotherm. A path or curve or its mathematical expression such that the temperature has a constant value.

Joule-Thomson Coefficient. The rate of change of temperature with change of pressure during the expansion of a gas at constant enthalpy.

Kieselguhr. A diatomaceous earth frequently used as a catalyst support or as an adsorbent and clarification agent.

Killed. The term describing a metal that has been deoxidized while molten, as by adding aluminum.

Lapped. A process of careful grinding and polishing which results in a close fit, as between a piston and cylinder.

LeChatelier's Principle. The principle or law which states that if a system is in equilibrium at a definite pressure, temperature, concentration, or similar condition and any one of these is changed, the state of the system will tend to change so as to counteract or reverse the change in condition. Thus, if the pressure is increased, the chemical equilibrium in the system will shift to yield a smaller volume and reduce the pressure.

Liquid-liquid Extraction. The transfer of a component in a liquid to another partially miscible liquid.

Make-up Gas. Fresh reactant gas added to the recycle stream of unreacted gas and fed to the reactor.

Manganin. An alloy of about 84 per cent copper, 4 per cent nickel, and 12 per cent manganese used for wire. The electric resistance is a linear function of pressure and is used for pressure gauges. See Sec. 5-1.

Mass-transfer Coefficients. A film coefficient for the transfer of mass between a fluid and a solid or liquid interface. See **Film Coefficient**.

McLeod Gauge. A special manometer connected to a gas reservoir and used to measure very low pressures (a vacuum gauge). The gas in the reservoir is compressed until its pressure can be measured by the manometer.

Natural Convection. The movement or circulation of a fluid resulting from density differences in the fluid. This is contrasted to forced convection, where the movement is caused by a pump or agitator.

Natural Gas. The product of gas wells drilled in the earth. It is frequently high in methane. The composition may vary widely. An example of such gas contains 96.0 per cent CH_4 , 3.2 per cent N_2 , and 0.8 per cent CO_2 .

Needle Valve. A valve having a stem with a long cone with a small cone angle so that the opening in the valve changes slowly as the valve handle is turned. It is useful in controlling the rate of flow through the valve.

Neoprene. A synthetic rubber made by polymerizing chloroprene. It is resistant to oil.

Nitration. The reaction which results in the substitution of a nitro group into an organic compound.

Noninductive Winding. A winding in which each turn of wire in one direction is matched by a turn in the opposite direction so the induction from a current in one is canceled by that from the other.

Non-Newtonian Fluid. Designation of a fluid with a viscosity that varies with the shearing stress on the fluid.

Normalizing. The heat treatment of a metal by heating for a relatively long time at lower temperatures (500 to 600°C) in a bath of fused salt or by cooling slowly from a high temperature in air.

Octane Number. A measure of the tendency of a fuel to knock or undergo premature combustion in an internal-combustion engine. The percentage of isooctane in a mixture with *n*-heptane when the mixture has the same combustion characteristics as the fuel in a standard engine.

Open System. A region with boundaries and with provision for a stream of matter to enter or leave the region.

Optical Flatness. A surface ground to specifications of flatness measured in terms of the wavelength of light and determined by an interferometer.

Packing. As a pressure seal, the material which surrounds and seals a moving shaft against leakage along the shaft. In a tower, the material of special shapes

such as short cylinders introduced to increase the surface of contact between a gas and a liquid or between two immiscible liquids.

Packing Gland. The space designed to contain the packing used to seal a moving shaft.

Partial Molal Volume. The rate of change in volume with change in the moles of one component in a mixture when all conditions such as temperature and pressure and the moles of all other components are held constant. This is the partial molal volume of the one component. The partial molal value of other extensive properties is defined similarly.

Partial Oxidation. An oxidation that is not carried to completion as when there is insufficient oxygen. In some reactions, carbon monoxide would be formed instead of carbon dioxide.

Partial Pressure. The pressure exerted by one component in a mixture of gases (see Sec. 8-14).

Perfect Gas. One which follows the perfect-gas law $pv = RT$. Real gases normally behave in this fashion as the pressure approaches zero and approximately at pressures up to 1 atm and higher. The internal energy depends on temperature only.

Perfect Solution. See **Ideal Solution**.

Per Pass. A term which refers to the passage of a reaction mixture once through a reactor. If the reaction is incomplete, the reactants may be separated from the products and returned to the reactor. Then the final yield is greater than the conversion per pass.

Phase Equilibrium. The condition which exists when two or more phases are in contact and there is no tendency for further changes in temperature, pressure, or composition to take place.

Piezometer. An instrument for determining the volume of a substance at various temperatures and pressures.

Plastic Deformation. The change in shape of a solid substance without fracture and in an inelastic manner.

Plastic Flow. The inelastic movement of one portion of a solid relative to another without fracture.

Platforming. A process for reforming hydrocarbon mixtures using a platinum catalyst.

Plunger. A rod which moves into and out of a cylinder through a packing gland but does not form a seal with the cylinder walls. This arrangement is effective in pumping a liquid or highly compressed gas by displacement.

Poiseuille's Law. The relationship which describes the isothermal nonturbulent flow of a Newtonian fluid through a cylindrical tube.

Poisoning. Permanent: contamination with a substance which reduces the activity of a catalyst and cannot be removed. Temporary: contamination with a substance which reduces the activity of a catalyst but is released from the catalyst when the contamination is removed from the stream passing over the catalyst. The catalyst then returns essentially to its original activity.

Polymerization. The process of forming complex, or high-molecular-weight, molecules by combining simpler, or low-molecular-weight, molecules. The term implies the capability of the combination of molecules proceeding indefinitely.

Potentiometer. An electric instrument used to measure or indicate small voltage drops. It is specially useful for the accurate determination of the voltages generated by thermocouples.

Producer Gas. The gaseous product of the burning of coal with a deficiency of air to yield CO instead of CO₂. Steam is usually added and reacts to form H₂ and

CO. A typical composition is 24 per cent CO, 16.5 per cent H_2 , 50.2 per cent N_2 , 7.5 per cent CO_2 , 0.6 per cent O_2 , and 1.2 per cent CH_4 .

Promoter. A substance without appreciable catalytic activity which serves to enhance appreciably the catalytic activity of another substance.

Pseudocritical Pressure. A pressure chosen to serve in place of the critical pressure for a mixture (see Sec. 8-14).

Pseudocritical Temperature. A temperature defined to serve in place of the critical temperature for a mixture. It differs considerably from the true critical temperature of the mixture (see Sec. 8-14).

Purge. A portion of the reacting gas mixture in a recycling system which is discarded in order to prevent the excessive accumulation of inert components.

Pyrolysis. A chemical process in which large molecules are broken down and rearranged to form smaller molecules by subjecting the mixture to high temperatures.

Quenching. The process of cooling suddenly, usually by immersing in a liquid when applied to steel or alloys, or by other means when applied to a reacting gas mixture. In the latter case, a liquid spray or a heat exchanger could be used to quench the reaction.

Raney Catalyst. A metal such as nickel in a finely divided form with extensive surface per unit weight prepared by dissolving the other ingredients in a nickel alloy.

Reactor. A vessel or enclosure in which a chemical reaction takes place.

Rectification. The separation of components in a volatile mixture by distillation and fractionation in a column.

Recycle. To return a portion of the product stream to a point upstream in the process.

Reduced Crude. The residuum left after the volatile components of crude petroleum oil have been removed by distillation.

Reduction. A chemical process in which hydrogen is added to, or oxygen removed from, a substance or in which the valence of an element in a compound is decreased.

Reentrant Cylinder. A cylinder constructed so that the fluid which exerts pressure on the inner wall exerts the same pressure on the outer wall (see Fig. 5-4).

Refinery Gas. The gaseous product of reactions in which liquid petroleum components are cracked and reformed. This gas contains a variety of saturated and unsaturated hydrocarbons and also hydrogen.

Reflux. The portion of the condensed liquid product from the top of a distillation column which is returned to the top of the column and flows down countercurrent to the rising vapors.

Reformer Furnace. A tubular reactor for petroleum components in which the hydrocarbons are cracked and react to yield a more desirable product such as one having a higher octane number. The reaction is endothermic, and heat is supplied through the walls of the tubes. Natural gas mixed with steam is reformed to produce hydrogen and carbon monoxide as a synthesis gas.

Repressuring Operations. The gas separated from the petroleum-gas mixture from an oil well is compressed and returned to the underground formation to aid in recovering a greater fraction of the liquid.

Rerun Stock. A liquid recovered from the product of a refining process and returned as feed to the process.

Residual Stresses. The stresses remaining in a solid body or vessel wall after it has been heat treated, subjected to internal pressure, or given some similar treatment and then returned to atmospheric pressure and temperature.

Residuum. The liquid or semisolid fluid remaining after the volatile components have been removed by distillation—a petroleum residuum, for example.

Resistance Thermometer. A wire whose electric resistance is measured and used to determine the temperature of the wire. The platinum resistance thermometer is used for very accurate temperature measurements.

Reversible Heat Engine. An ideal concept used in thermodynamics but not actually attainable. In such an engine, work could be done on the engine to raise the temperature level of a quantity of heat, and the process could then be completely reversed, the temperature level of the heat being lowered and the original amount of work being done by the engine.

Rimmed Steel. Unkilled steel, or steel that has not been deoxidized in the molten state.

SAE 6150. A classification of carbon and alloy steels by the Society of Automotive Engineers and also by the American Iron and Steel Institute (AISI). The first digit indicates the type of steel; the second, the percentage of the major alloying element; and the last two, the hundredths of a per cent of carbon in the steel.

Saponification. Originally the hydrolysis of fats with an alkali to form soap. It now relates in general to the hydrolysis of an ester in an alkaline solution to yield an alcohol and a compound of the remaining part of the ester.

Saturation. The extent to which a gas contains a partial pressure of a volatile component, such as water, approaching the vapor pressure of the component. Per cent saturation is the ratio of the partial pressure to the vapor pressure times 100.

Sauereisen. Trade name for a magnesite-base cement resistant to acids, water, oil, most solvents, and electricity for temperatures up to about 1100°F.

Score. To scratch or notch.

Seat. The part of a valve against which the stem rests when the valve is closed.

Semipermeable Membrane. An ideal concept used in thermodynamics for a membrane which permits the free passage of one type of molecules and serves as a complete barrier for others.

Shift Converter. A reactor in which the water-gas-conversion (or shift) reaction takes place. Steam and carbon monoxide are converted to hydrogen and carbon dioxide.

Side Reactions. The reactants form products other than the products of the principal reaction.

Silver Solder. Alloys containing from 5 to 80 per cent silver with melting points from about 250 to 800°C and used as solder.

Sintering. A metallurgical process for bonding small pieces together at the points of contact to make large pieces by the action of heat causing partial fusing and recrystallization.

Sites on a Catalyst. Molecules or points on a catalyst surface which have a special orientation or configuration such that they are active in causing a chemical reaction to take place.

Space Lattice. The regular pattern in three dimensions in which the molecules of a crystal are arranged.

Space Velocity. The ratio of volume (STP) rate of flow of gas through a catalyst bed to the volume of the bed, usually expressed as $\frac{\text{cu ft/hr}}{\text{cu ft}} = \frac{1}{\text{hr}}$.

Spark Welding. A method of electric welding.

Stabilizer. A distillation or absorption column for removing the more volatile components from a petroleum mixture or solvent.

Stage. A step in the increase in pressure produced by a single cylinder of a compressor. The gas flows through several cylinders or stages when its pressure is increased from a low to a high value.

Standard State. The defined condition of a substance or system serving as a reference state. Values of properties are stated as a change from this state.

Statistical Mechanics. A method of treating the mechanical behavior of an assemblage of a very large number of molecules on a statistical basis.

Stem. The moving part in a valve which closes against the seat.

Strain. The change in dimensions of a body. Linear strain is change in length per unit length.

Strain Gauge. A gauge for measuring a change in dimension. One type depends on stretching a wire fastened to the body and noting its change in electric resistance.

Stress. A force per unit area.

Stuffing Box. A sealing arrangement for holding packing against a moving rod where it enters a cylinder or chamber in order to prevent leakage from the chamber along the rod.

Swage. To bend or shape cold metal to a required form by means of a tool, die, or stamp.

Synthesis Gas. The gas mixture fed to a reactor in any process which carries out a gaseous reaction such as the synthesis of ammonia or methanol.

Synthesis Loop. The circuit made by the reactant gases recovered from the product from a synthesis reactor and returned to pass again through the reactor.

System. A substance or mixture and sometimes its container or other accessories as defined or identified for use in determining energy changes and similar variations.

Teflon. Polymer of tetrafluoroethylene stable to 500°F and inert to most solvents and reagents; useful as a material for gaskets in high-pressure apparatus.

Tempering. A term applied to a process for treating metals consisting of heating and cooling at predetermined rates and temperatures used to obtain the desired toughness and hardness.

Thermal Coefficient of Linear Expansion. The change in length of a body per unit length per degree of temperature, or $\frac{1}{L} \frac{dL}{dt}$.

Thermal Conductivity. The amount of heat conducted through a body per unit time per unit area per unit temperature gradient.

Thermal Cracking. The process of splitting molecules, usually hydrocarbons, by raising their temperature until they break apart.

Thermal Expansion. The increase in dimensions of a body or in the volume of a gas accompanying an increase in temperature.

Thermal Fatigue. The decrease in strength of a body due to repeated temperature cycles.

Thermodynamic Potential. The partial molal free energy of each component of a mixture. This is the same in two phases which are in equilibrium, for instance.

Thermodynamic Reversibility. An ideal concept which requires that all changes in a system may be reversed and the system returned to its initial state without leaving any residual changes in the system or its surroundings.

Transducer. An instrument for measuring small displacements or forces as an electric-current output.

Transport Properties. Viscosity, thermal conductivity, molecular diffusivity, and similar properties related to the irreversible transport of momentum, heat, matter, and the like by intermolecular transfer.

Triple Point. The three-phase equilibrium for a pure substance where vapor, liquid, and solid coexist.

Triplex. An arrangement in a pump of three cylinders which are coordinated and operated in parallel to provide a more uniform flow.

Tube Sheet. The metal plate drilled with holes into which tubes are rolled, such as at each end of a tubular heat exchanger.

TVA. Abbreviation for Tennessee Valley Authority.

Unit Operations. A term used in chemical engineering for the steps in an industrial chemical process which involve physical changes and separations rather than chemical reaction. Examples are distillation, filtration, and absorption.

Unit Processes. A term used in chemical engineering for the steps in industrial chemical processes which involve a chemical reaction classified according to the type of chemical reaction. Examples are alkylation, hydrogenation, and sulfonation.

Units. The defined amounts of kinds of quantities used to measure various amounts of these quantities.

Unit Strain. Elongation per unit of length—usually per unit of original length.

U Tube. A tube in the shape of a U frequently used as a manometer or with mercury to separate a gas from a liquid in an experimental system.

Wet-test Meter. A type of meter which measures the volume of gas passed through it and uses a water seal to enclose the rotating member.

Work Hardening. The hardening and increase in yield strength caused by deformation (or working) of a metal.

X-ray Diffraction. The scattering or diffraction of X rays passed through a solid. The diffraction pattern indicates whether the molecules are arranged in a regular space lattice as in a crystal or randomly as in an amorphous solid.

Yield. The amount of product obtained from a chemical process, usually as a percentage of the amount theoretically possible if all the reagents originally present were converted in the proper stoichiometrical ratios. The yield may be obtained from several passes through the reactor.

Yield Strength. A stress as indicated on the stress-strain diagram when the strain reaches a predetermined value (see Sec. 3-1).

Yield Point. The stress as shown on a stress-strain diagram where the metal suddenly stretches, as in low-carbon steels (see Sec. 3-1).

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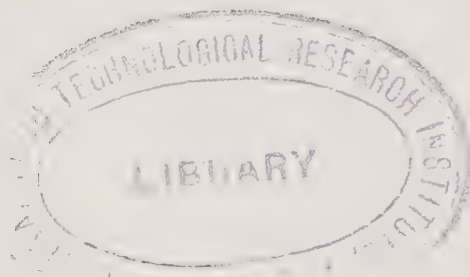
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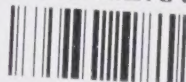
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